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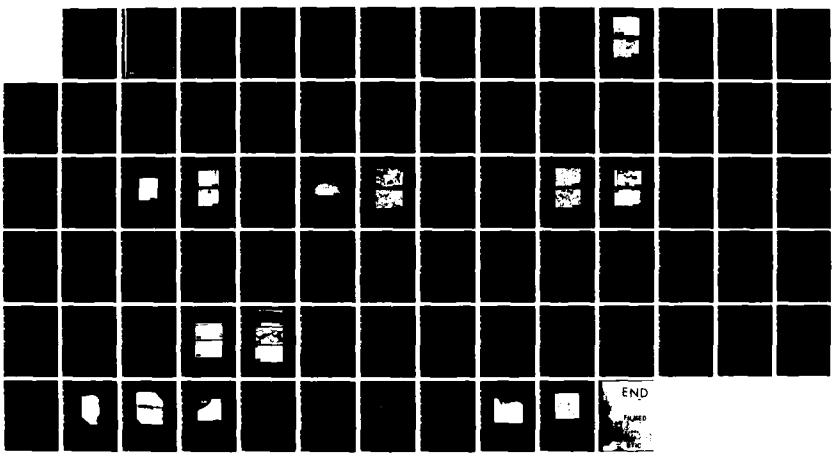

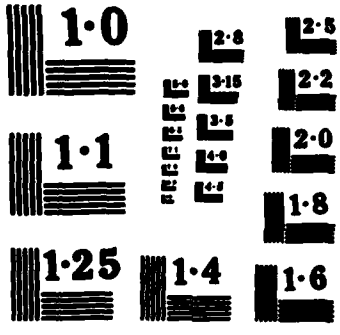
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SILICON NITRIDE JOINING

Annual Report

May 1984

By: Sylvia M. Johnson and David J. Rowcliffe

Prepared for:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
Department of the Air Force
Bolling Air Force Base, DC 20322

Attention: Capt. J. Hagar
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Contract No. F49620-81-K-0001

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The results obtained in the third year of a continuing investigation into a method of joining silicon nitride with an oxide glass are described. Mechanical behavior of joints at room temperature and the criteria for strong joints are detailed (Appendix A). Two approaches were taken to strengthen the joints: heat treatments to crystallize the glass in the joint and surface preparation. The high temperature behavior of various Si_3N_4 glass systems was investigated by means of high temperature mechanical tests, mass spectrometry, theoretical calculations, and mass transport studies (Appendix B). Alkali and alkaline earth species present in Si_3N_4 or in the glass were found to be deleterious to joint integrity. The results of all transmission electron microscopy studies performed are included as Appendix C to this report.

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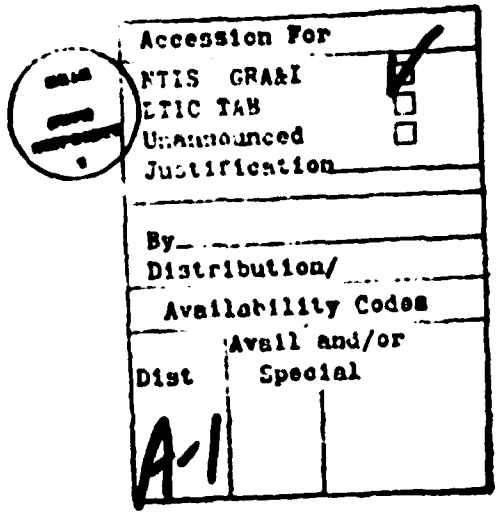
SCIENTIFIC CONTRIBUTIONS

The project leader is David J. Rowcliffe. Studies of the mechanical and high temperature behavior of the joint system were performed by Sylvia M. Johnson. Mass spectrometry studies were conducted by Robert D. Brittain and the theoretical calculations were performed by Robert H. Lamoreaux. TEM studies were performed by Martha L. Mecartney at Stanford University under the supervision of Robert Sinclair.



INTRODUCTION

Structural ceramics have a wide variety of potential uses that range from low temperature, relatively low stress applications in wear resistant parts to high temperature, high stress applications in advanced heat engines. However, before the full potential of ceramics can be realized, new or improved methods of fabricating components and systems must be developed. Methods of joining ceramics are of particular interest, especially for applications where a joint must have a high strength at high temperature. Silicon nitride is being considered for use in the most demanding applications, and thus a method of reliably joining Si_3N_4 is required.

SRI International has devised a new method of joining Si_3N_4 that is based on the controlled reaction between an oxide glass and Si_3N_4 and has been investigating the method and the system under AFOSR sponsorship. The results obtained during the third year of this investigation are presented in this report.

During the first two years a simple, pressureless method of joining Si_3N_4 was developed. Research during the first year[1] concentrated on determining the joining procedure, the range of joining conditions, and TEM studies of the interfacial region. During the second year[2] the joining procedure was refined with the addition of a glazing step, and the mechanical behavior at room temperature was investigated. The joints have strengths at room temperature that are substantially higher

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[1] R. E. Loehman, M. L. Mecartney, and D. J. Rowcliffe, "Silicon Nitride Joining," AFOSR Annual Report, Contract F49260-81-K0001, February 1982.
[2] S. M. Johnson and D. J. Rowcliffe, "Silicon Nitride Joining," AFOSR Annual Report, Contract F-49620-81-K0001, March 1982.

than any previously reported.[3] The mechanisms of fracture and requirements for strong joints are understood. The strength is constant over a range of joining conditions (1575°-1650°C and 30-60 minutes) and is independent of the nitrogen overpressure. The joint thickness determines the joint microstructure, which in turn, determines the strength. Maximum strength, ~ 460 MPa, is achieved with joints that are 20-30 μm thick. The explanation of the strengthening mechanism in joined Si_3N_4 was the starting point for the research of the third year.

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[3] P. F. Becher and S. A. Halen, "Solid-State Bonding of Si_3N_4," Bulletin, of The American Ceramic Society 58, 584-486 (1979).

TECHNICAL PROGRESS

Progress during the third year of the program is summarized below. The experimental procedures are discussed in more detail in Appendices A and B.

Research during the third year had two objectives: first to investigate the high temperature behavior and, second, to strengthen existing joints. Initially, bend tests were performed in air at temperatures up to 1300°C on Si_3N_4 joined with a $MgO-Al_2O_3-SiO_2$ glass, HN-9M, and with an yttrium oxynitride glass, SG-14. However, the strength of joined bars tested under these conditions was very low. Joints that were originally up to ~ 60 μm thick expanded to ~ 1 mm. This expansion destroyed the integrity of the joint and the bars fell apart under their own weight. The joint expansion was worst in the samples that were joined with the oxynitride glass. The glass in these joints bubbled extensively and ran out of the joint onto the side of the bar.

Two approaches were taken to improve the strength of the joints. First, an additional step was added to the joining method to ensure that the joints were uniform. Strength depends on joint thickness, and a uniform joint thickness is desirable for controlled strength (see Appendix A). All surfaces were either lapped or polished flat before joining. Second, the samples were heat treated after joining to promote crystallization in the joint. Crystallization treatments were performed in ~ 200 kPa N_2 at 1100°-1300°C for 1-2 hours. The strength of heat-treated samples was ~ 50% that of nonheat-treated samples. Examination of the fracture surfaces of heat-treated samples indicated that large voids had formed during the heat treatment, so that the glass phase was present as "islands" rather than as the original complete layer. A

complete discussion of the joining parameters and their effect on mechanical properties is given in Appendix A.

The results of the high temperature strength measurements and of the crystallization treatments indicated that vaporization and mass transport reactions were occurring. This conclusion was also supported by the observation that joining times of > 90 minutes resulted in joints with very low strengths, or disappearance of the glass and consequently no joint.

A mass spectrometry study was instigated to determine the vaporization behavior of these materials and systems. Mass spectrometry was performed on the glasses, on two grades of Si_3N_4, and on Si_3N_4 glazed with the glasses. The results of the mass spectrometry study are presented in detail in Appendix B. The results of the mass spectrometry study in conjunction with some additional experiments in which Si_3N_4 and glazed Si_3N_4 were heat treated in N_2 to study mass transport have important implications for joining, sintering, and long-term exposure of Si_3N_4 to high temperatures.

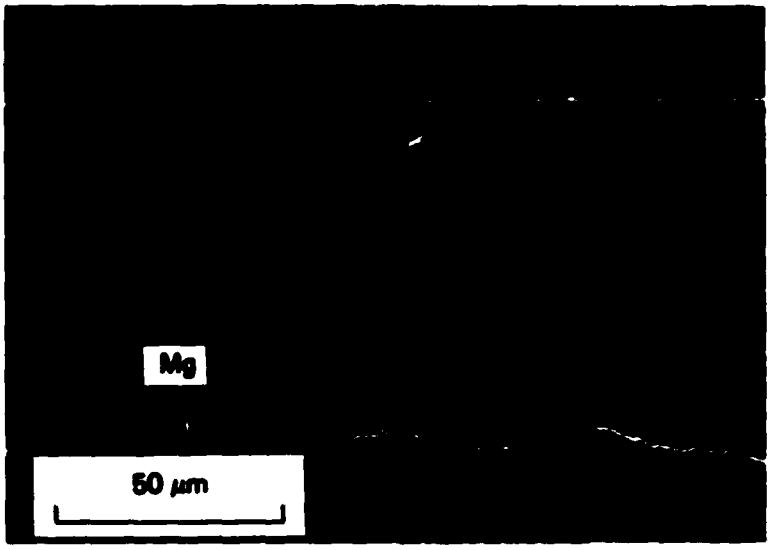
Alkali and alkaline earth species were found to have very high vapor pressures. These species include Mg, which is commonly added as a sintering aid, and impurites such as Na, Ca, and K. The vapor pressures of these elements are significant even when they are only present as impurities. In contrast, amphoteric species, such as Y and Al, were not detected in the vapor. Theoretical calculations indicated a strong dependence of partial pressures of the various species on oxygen potential. In particular, Na, Mg, and SiO have very high vapor pressures under reducing conditions.

Heat treatments were performed on Mg-doped Si_3N_4 (NC132) glazed with an Y_2O_3-Al_2O_3-SiO_2 glass (SC-14-0) to study mass transport in the system. The appearance of a sample treated for 165 minutes in an overpressure of 6.7 atm of N_2 at 1100°C indicated that significant mass transport had occurred. Mg could not be detected in significant amounts in the glass in the sample immediately after glazing. However, after heat treatment an EDAX scan showed that Mg had diffused from the Si_3N_4

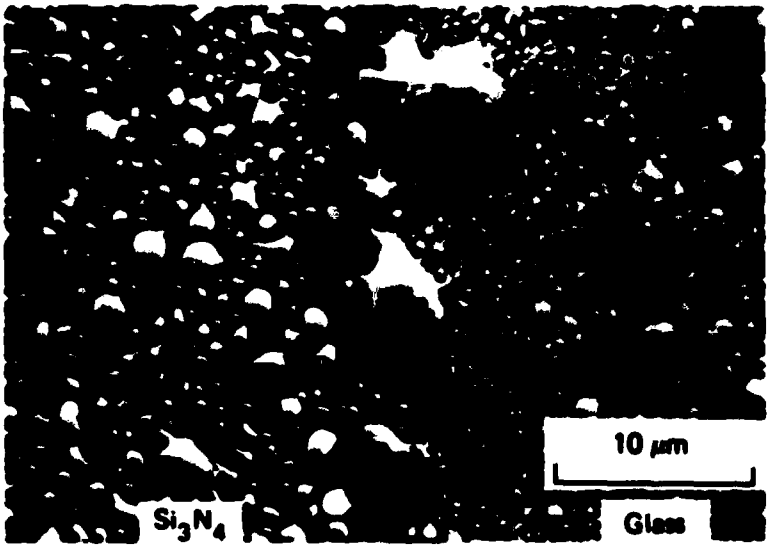
to the outer edge of the glass layer [Figure 1(a)] The surface of the sample, which was polished before the heat treatment, showed considerable evidence of transport from the interior of the Si_3N_4 to the interface and to the surfaces of both the Si_3N_4 and the glass [Figure 1(b)]. Large globules of a glassy phase exuded from the interface, and smaller exudates were present on the surfaces of the Si_3N_4 and the glass. Examination of the interior of the glazed region revealed the presence of bubbles in the glass similar to those observed in mass spectrometry samples (see Appendix B).

The evidence from the high temperature strength measurements, mass spectrometry, theoretical calculations and mass transport studies indicates that mass transport is a serious problem in systems that contain alkali or alkaline earth oxides. Mass transport and the associated vaporization cause degradation of the surface, glass-Si_3N_4 interface, and the joint. Mass transport to the surface or to the glass will occur regardless of the atmosphere because the interior of the Si_3N_4 is very much more reducing than any glass or surface. An important conclusion is that joining systems that contain alkali or alkaline earth oxides are not suitable for use at high temperatures. However, joints made by this method still have potential for use at temperatures below ~ 1000°C.

The results of all the transmission electron microscopy studies performed during the first three years of the program are summarized in Appendix C. This part of the program provided detailed information on several aspects of the microstructures and compositional changes that occur in joints. Energy dispersive spectroscopy was used to determine the compositions of grain boundary phases in NC132, so that joining glasses of similar composition could be made. Reactions between Si_3N_4 and glass melts were studied using TEM and X-ray diffraction techniques. These studies demonstrated the formation of Si_2N_2O at the Si_3N_4/glass boundary and also showed the extent to which the original Si_3N_4 surface dissolves during joining. Crystallization of Mg-containing glasses occurs through the precipitation of $MgSiO_3$ and spontaneous crystallization was observed in scandium-containing glasses used for tracer experiments.



(a) Mg Scan



(b) Interfacial Region

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FIGURE 1 EDAX SCANS OF Mg-DOPED Si_3N_4 (NC132) GLAZED WITH Y_2O_3-Al_2O_3 GLASS (SG-14-0) AFTER HEAT TREATMENT IN 6.7 atm N_2

(a) Mg scan across NC132
(b) Interface between NC132 and SG-14-0

FUTURE WORK

The following research tasks will be undertaken during the fourth year of this research program:

(1) Optimize the joining glass composition to minimize vaporization. This task entails fabrication of very pure glasses containing less volatile oxide species.

(2) Investigate the vaporization behavior of several silicon nitrides, including chemical vapor deposited (CVD) Si_3N_4 and materials with very low or controlled impurity contents.

(3) Determine the maximum use temperature of joined ceramics using one or more glasses from Task 1 and a silicon nitride from Task 2. The strength and vaporization behavior at various temperatures up to 1000°C will be investigated.

(4) Investigate a method of joining β-Si_3N_4 coated with thin layers of α- or amorphous-Si_3N_4 and oxides. Various combinations of α-Si_3N_4/oxide coatings and the effects of both low and high temperature strengths and fracture mechanisms will be investigated.

PUBLICATIONS AND PRESENTATIONS

Publications

1. R. D. Brittain, S. M. Johnson, R. H. Lamoreaux, and D. J. Rowcliffe, "High Temperature Chemical Phenomena Affecting Silicon Nitride Joints," to be published in J. Am. Ceram. Soc., August 1984.

2. S. M. Johnson and D. J. Rowcliffe, "Mechanical Properties of Joined Silicon Nitride," to be submitted to J. Am. Ceram. Soc.

Presentations

1. S. M. Johnson and D. J. Rowcliffe, "Fracture Mechanisms of Joined Silicon Nitride," Annual Meeting of the American Ceramic Society, Chicago, IL (April 1983).

2. M. L. Macartney, D. B. Marshall, and S. M. Johnson, "Fracture Toughness of Joined Si_3N_4," Annual Meeting of the American Ceramic Society, Chicago, IL (April 1983).

3. S. M. Johnson and D. J. Rowcliffe, "High Temperature Behavior of Joined Silicon Nitride," Pacific Coast Regional Meeting, American Ceramic Society, San Diego, CA (October 1983).

4. M. L. Macartney, R. Sinclair, and R. E. Loehman, "Properties and Reactivity of Simulated Si_3N_4 Grain Boundary Phases," Pacific Coast Regional Meeting, American Ceramic Society, San Diego, CA (October 1983).

5. S. M. Johnson, "Silicon Nitride Joining," Materials Research Seminar, SRI International (March 1984).

6. S. M. Johnson, R. D. Brittain, R. H. Lamoreaux, and D. J. Rowcliffe, "Vaporization Processes in the Joining of Silicon Nitride," Annual Meeting of the American Ceramic Society, Pittsburg, PA (May 1984).

Appendix A

MECHANICAL PROPERTIES OF JOINED SILICON NITRIDE

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ABSTRACT

A technique is described to join Si_3N_4 ceramics using oxide glasses. The technique involves a glazing step, followed by a pressureless reaction treatment of 30-60 minutes at 1575°-1650°C. The reactions between the glasses and Si_3N_4 are reported. An important event is the dissolution of Si_3N_4 and the growth of Si_2N_2O crystals into the joint. The strength of joined bars depends on the joint thickness. Two strength regimes are identified and two corresponding fracture mechanisms are described. A maximum strength of ~460 MPa is achieved for joint thickness of ~30 μm.

This work was supported by the Air Force Office of Scientific Research under Contract F49620-81-K-0001

I. INTRODUCTION

Until recently, relatively little attention has been paid to joining of ceramic parts to other ceramics or to metals for structural applications. However, the role of ceramics in developing new energy-efficient systems and components has led to a realization of the increasing importance of developing new joining technologies. Potential applications for ceramic/ceramic or ceramic/metal joining include heat engines, heat exchangers and recuperators, and burners.

Joining is important in the fabrication of large structures for two reasons: processing and reliability. Processing of large, complex shapes is both difficult and expensive. Hot pressing is limited to relatively small, simple shapes. Sintering and hot isostatic pressing require an initial forming step, e.g., cold pressing, slip casting, or injection molding, which also restricts the shape and size. Although complex shapes, such as turbine rotors, can be made with these techniques, reliable methods of joining are still required to assemble complete systems.

Reliability of ceramic structures is probably the major concern of manufacturers and users of structural ceramics.[1] Joining smaller pieces to make a large structure might improve reliability. A crack propagating through a monolithic structure can cause catastrophic failure of the entire piece, whereas failure in a joined structure may be limited to one section which can be replaced. Also, the difficulties involved

in processing large, monolithic structures invariably result in larger flaw populations. Smaller pieces may be tested and substandard parts rejected at a much lower cost.

There is no universal method analogous to metallurgical welding for joining two dissimilar or even similar ceramic materials. Brazing with metal alloys that wet Si_3N_4 has been used to join Si_3N_4.[2,3] Such joining methods are limited to relatively low use temperatures because the metal alloys used tend to be less refractory and corrosion resistant than the Si_3N_4. Reaction-bonded Si_3N_4 has been joined[4] by nitriding a layer of silicon deposited between the parts. The joint formed is porous and the method is not suitable for joining hot-pressed or sintered Si_3N_4. Components have also been fabricated from two pieces by hot pressing with an intermediate powder layer.[5] Becher and Halen[6] hot pressed Si_3N_4 pieces using a layer of ZrO_2 powder and a pressure of less than 1.5 MPa. Room temperature strengths of up to 175 MPa were obtained using this method.

In the work described here, hot-pressed Si_3N_4 is joined with an oxide glass. The original concept[7] was based on duplicating the structure of hot-pressed or sintered Si_3N_4 where Si_3N_4 grains are essentially surrounded and held together by a second phase. This second phase is an oxynitride glass formed by reaction between hot pressing additives (e.g., Al_2O_3, MgO, Y_2O_3) and Si_3N_4. Dissolution of Si_3N_4 in the oxide glass used in this work should result in an oxynitride glass with a composition similar to the grain boundary phase in hot-pressed Si_3N_4, and the resulting joint should resemble a large grain boundary.

The actual reactions that occur are slightly more complex than those first envisioned because Si_3N_4 dissolves in the glass and silicon oxynitride precipitates. However, such joints are strong at room temperature, and the chemistry of the joint and mechanisms of fracture at room temperature are discussed in this paper. High temperature behavior is discussed elsewhere,[8] as is the detailed chemistry of the glass-Si_3N_4 reaction.[7,8]

II. EXPERIMENTAL TECHNIQUES

(1) Materials

Two billets of hot-pressed Si_3N_4 (NC132-I and NC132-II) and one joining composition (HN-9M) were used in most tests. The major impurities in the NC132 billets are listed in Table I. NC132-II was used in most strength tests.

The nominal glass composition (HN-9M), selected to be similar to that found at the grain boundaries of NC132, was as follows: SiO_2, 54.97 wt%; MgO, 35.27 wt%; and Al_2O_3, 9.66 wt%. The composition of the glass was determined by EDAX and by calculation from the chemical analysis.[9]

(2) Joining Experiments

The sample configuration used initially consisted of two Si_3N_4 plates separated by powdered glass and supported in a boron nitride jig (Fig. 1). This configuration produces a simple end seal. The technique has been refined to a two-stage process: an initial glazing step

followed by the joining operation, which provides more precise control over the joint thickness.

Samples are cleaned in trichlorethylene, acetone, and methanol, and a slurry of the powdered (-100 mesh) glass is applied to one piece. Glazing is performed in a graphite furnace under ~200 kPa N_2, and temperatures are measured with a Pt-Pt 10% Rh thermocouple. The heat treatment for glazing consists of 15 minutes at 1480°C followed by 10 minutes at 1620°C. This temperature profile resulted in a uniform layer of glass on Si_3N_4. The glazed end is ground down until only a thin layer of glass remains, and the glazed piece is then placed above an unglazed piece for joining. Although the amount of glass left on the glazed piece depends on the desired joint thickness, it is important that the layer be flat and that the pieces are ground until this condition is reached.

Crystallization treatments were performed on selected joined samples immediately after joining.

(3) Mechanical Tests

Joined bars were surface ground and cut into bend test bars ~50 mm by 3 mm by 3 mm. Some bars were diamond polished to 1 μm on one face, and edges of all bars were bevelled to remove corner cracks. Joint thicknesses were measured in three places in each sample. Samples were broken in a four-point bend configuration, with the polished faces in tension, at a displacement rate, $\dot{D}$, of 0.5 mm/min.

(4) Microscopy

The joint region in both broken and unbroken bars was examined using SEM. Both the fracture and tensile surfaces of broken bend test bars were studied. Several joint regions were examined by transmission electron microscopy (TEM) and chemically analyzed using an energy dispersive X-ray system (EDAX). The results of the TEM studies on this system are reported elsewhere.[7]

III. RESULTS

(1) Joining Experiments

Examination of the earliest joints produced showed that the thickness of the joined region varied between about 5 and 100 μm, depending on the quantity of glass and the specific joining conditions. Better control of the joining process was achieved when one Si_3N_4 piece was glazed.[10] The glazed layer was then ground down to ensure a plane surface and a minimal amount of glass. However, if all the glass on the surface is removed, leaving only the glass that has penetrated the grain boundaries, the pieces do not join. A minimum amount of glass in the joint is therefore necessary for joining because the glass will not flow out of the grain boundaries.

Part of a very thin (~ 5-μm) joint is shown in Fig. 2. The tungsten particles, which appear as white spots in optical and SEM micrographs and as black spots in TEM micrographs, were analyzed by EDAX and contained W, Si, Fe, Co, Cr, and Mn in varying amounts.[7] Similar particles are found in NC132 hot-pressed Si_3N_4 and are known to

originate from the WC balls used to mill the powders before hot pressing.

Both the glazed layers and the joints contained arrays of cracks normal to the interface; these cracks are caused by differences in thermal expansion coefficients. Silicon nitride has a thermal expansion coefficient, α, of ~3.2 x 10^{-6} °C, whereas HN-9M glass has a thermal expansion coefficient of ~5.96 x 10^{-6}/°C.[11] The variation in the thermal expansion coefficient of HN-9M glass with Si_3N_4 content indicated only a weak dependence of α on the nitrogen content.[11] The coefficient was reduced to ~ 5.2 x 10^{-6}/°C in a glass containing 4.3 at.% nitrogen.

The possibility that this difference in expansion coefficients can cause thermal fracture can be estimated as follows. The strain, e, developed as a result of the mismatch is:

$$e = \Delta\alpha\Delta T \qquad (1)$$

With $\Delta T \approx 1000$ K and $\Delta\alpha \approx 2 \times 10^{-6}$/°C, then $e \approx 2 \times 10^{-3}$. The Young's modulus of HN-9M glass was determined by an acoustic resonance technique to be 140 GPa.[7] The stress, σ_α, that develops in the glass as a result of the thermal expansion difference, is thus ~280 MPa. The strength of the glass at room temperature was measured to be ~175 MPa. Therefore, the thermal expansion mismatch stress is sufficient to cause the observed cracking.

Examples of thermal expansion mismatch cracks are shown in Fig. 3. The cracks are perpendicular to the plane of the joint and develop

in the glass and extend across even very thick joints. Very thin joints, < ~5 μm, are not so extensively cracked. The traces of these cracks can be seen on fracture surfaces where the glass has broken into many small pieces (Fig. 3). The cracks, represented schematically in Fig. 4, extend into the transition zone, which contains a large amount of glass. There are no cracks parallel to the joint because the upper Si_3N_4 piece is free to move and relieve any stresses perpendicular to the joint. The glass is not as hard or as tough as the Si_3N_4 and tends to chip out along these cracks during grinding. The cracks and their role in the fracture process are discussed in more detail below.

(2) Glass-Si_3N_4 Reactions

The reaction between the glass and the Si_3N_4 appears to proceed as previously described:[9,11] glass penetrates the Si_3N_4 grain boundaries, and Si_3N_4 dissoves in the glass. Silicon oxynitride crystallizes from the glass as increasing amounts of Si_3N_4 dissolve.

Si_2N_2O crystals were observed using SEM. Figure 5 shows the polished, tensile surface of a broken bend bar. The light crystals growing into the glass from the Si_3N_4 are similar to crystals identified as Si_2N_2O by EDAX.[9] Large glass pockets are also evident in the interfacial region. Tungsten particles, which indicate the original position of the interface, can be seen in the glass above the level of the Si_2N_2O crystals, indicating the extent of Si_3N_4 dissolution.

The interlocking nature of the Si_2N_2O crystals is shown in Fig. 6, a micrograph of part of the fracture surface through a thin joint. Very little glass remains, and the Si_2N_2O layer is very porous. This is a

result of the ~12%-15% volume change associated with Si_2N_2O crystallization and removal of the glass by diffusion along the grain boundaries in the Si_3N_4. The volume change results from the difference in densities between Si_2N_2O[12] (~2.87 g/cm^3) and oxynitride glasses[13] (~2.6/cm^3). As Si_2N_2O crystals grow, holes form in the surrounding glass. Part of the fracture path through Si_3N_4 is also shown in Fig. 6 for comparison.

(3) Mechanical Tests

Four-point bend tests were used to determine the strength of joints from the first experiments and to define a set of optimum joining conditions. Various glass compositions and two silicon nitrides were used in these initial tests. The joint thickness was not controlled in these early experiments, nor were the test bars polished. The results of the initial strength survey are shown in Fig. 7.[7] Only the maximum strengths obtained are plotted because these represent the best strengths attainable. However, within the optimum range of joining conditions, 1575-1650°C and 30-60 minutes, the strengths are clustered at ~400 MPa and do not appear to depend on the specific joining conditions. Outside the optimum range, the strengths are very low and bars break during normal handling. The strength of Si_3N_4 bars is ~725 MPa and of glass bars is ~175 MPa.

Because the maximum strengths appeared to be independent of joining conditions, one set of joining conditions (1580°C for 45 minutes) was chosen for strength tests. Joined bars were polished to 1 μm. Joint thickness can be more easily measured on polished surfaces, and the joint region can be examined by SEM. Several bars were joined under

identical conditions and polished, and their strengths were measured. The fracture and tensile surfaces of several of bars were examined by SEM. The fracture origins were nearly always subsurface, and there was no difference in strength between polished and ground samples.

The fracture strengths, as a function of joint thickness, are plotted in Fig. 8. The shape of the strength-joint thickness curve suggests that there are two fracture mechanisms. The strength increases with joint thickness from joint thicknesses below ~20-25 μm and decreases with increasing joint thickness above ~35 μm. The strength is relatively constant within the transition zone of ~25-35 μm. The maximum strength achieved is ~460 MPa.

IV. DISCUSSION

(1) Mechanisms of Fracture

SEM examination of the fracture surfaces indicates that there are indeed two fracture mechanisms corresponding to the two strength regimes. If a joint is very thin, < ~25 μm, Si_2N_2O crystals will grow across the joint and form an interlocking array. However, the glass is consumed during crystal growth, and the resulting structure is very porous, as is shown in Fig. 6. Fracture initiates in the Si_2N_2O layer, and the crack travels through the Si_2N_2O, the interface, and the Si_3N_4. The strengths are low as a result of the porosity of the interfacial layer. As the joint thickness increases, more glass will remain between the Si_2N_2O crystals. An example of the microstructure of a higher strength joint is shown in Fig. 9, where Si_2N_2O crystals have grown in

the glass. However, some areas are becoming porous as the glass is consumed. The low strength of very thin joints can probably be attributed to incomplete glass coverage of the Si_3N_4 and the subsequent formation of large voids in the joint.

Thicker joints, > ~35 μm, contain more glass, and Si_2N_2O crystals are unable to grow completely across the joint. Si_2N_2O crystals do grow across the Si_3N_4-glass interface, resulting in a strong interfacial bond. The layer of glass in a thick joint cracks as a result of the thermal expansion mismatch. These cracks run through the interface, but penetrate only a short distance into the Si_3N_4. Large glass pockets are present in the Si_3N_4 near the joint,[9] and the cracks extend only into these regions.

The thermal expansion cracks illustrated in Fig. 4, allow the formation of many essentially independent fracture origins. The independent fracture initiation sites are often bubbles or pores in the glass. Cracks grow across each of these areas but stop at the thermal expansion cracks. Eventually, many adjoining areas fracture and catastrophic failure occurs. When a developing crack intersects a preexisting crack, it tends to restart at the ends of that crack and to continue through the Si_3N_4. Higher strengths are associated with a major portion of the crack path running through the Si_3N_4. Figure 10 shows an example of a high-strength sample where the fracture origin is in the glass but the fracture path is mostly through Si_3N_4.

There is a transition region where the two fracture mechanisms occur simultaneously; i.e., some areas of the joint are cracked and others only have Si_2N_2O crystals present. An ideal joint would have

Si_2N_2O crystals growing across the joint but in a glass matrix. However, a joint microstructure of this type will form only within a very limited joint thickness range; thus, control over the amount of glass used in glazing and joining is critical. However, a range of joint thicknesses for a desired strength can be defined from the present results; i.e., within certain minimum and maximum thickness limits, the joint will have a certain strength regardless of the pertinent fracture mechanism.

V. CONCLUSIONS

A preliminary survey of joint strength indicated that the strength was independent of the joining time and temperature within the optimum range of 30-60 minutes and 1575°-1650°C. Two fracture modes were identified by SEM and linked to the joint thickness and extent of interfacial reaction. The thermal expansion mismatch between the glass and Si_3N_4 and the resulting cracks appeared to influence the fracture process greatly. The original concept of forming a thin joint analogous to a grain boundary is not entirely correct because very thin joints are incomplete and weak. Silicon oxynitride crystals, not silicon nitride crystals grow across the joint, forming an interlocking but porous structure. In strong joints, cracks are stopped or deflected into the Si_3N_4 by thermal expansion cracks.

The maximum strength achieved is ~460 MPa, a substantial fraction of the strength of monolithic pieces. This is the best strength that has been reported for joined Si_3N_4. The method has the added advantage

of being simple and has potential for use as a method of joining Si_3N_4 for structural purposes.

REFERENCES

[1] D. J. Rowcliffe and S. M. Johnson "GRI High Temperature Ceramics Workshop," GRI Report, to be published (1984).

[2] H. R. Heap and C. C. Riley, "Method of Brazing," Brit. Pat. No. 1,310,997, March 21, 1973.

[3] A. J. Sorrell, "Method of Brazing Ceramic Articles to One Another," Brit. Pat. No. 1,387,478, March 19, 1975.

[4] R. S. Wilks, "Improvements in or Relating to Joining Silicon Nitride to Silicon Nitrides," Brit. Pat. No. 1,417,169, December 10, 1975.

[5] M. V. Goodyear and A. Ezis, "Joining of Turbine Engine Ceramics," in Advances in Joining Technology; pp. 113-153. J. J. Burke, A. E. Gorum, and A. Tarpinian, Eds., Brook Hill Pub. Co., Chestnut Hill, May 1976.

[6] P. F. Becher and S. A. Halen, "Solid-State Bonding of Si_3N_4," Amer. Ceram. Soc. Bull. 58, 584-586 (1979).

[7] M. L. Macartney, R. E. Loehman, and R. Sinclair, "Silicon Nitride Joining," submitted to J. Am. Ceram. Soc.

[8] R. D. Brittain, S. M. Johnson, R. H. Lamoreaux, and D. J. Rowcliffe, " High Temperature Chemical Phenomena Affecting Si_3N_4 Joining," to be published in J. Am. Ceram. Soc., August 1984.

[9] R. E. Loehman, M. L. Macartney, and D. J. Rowcliffe, "Silicon Nitride Joining," AFOSR Annual Report, Contract F49620-81-K0001, February 1982.

[10] R. E. Loehman, Private Communication.

[11] S. M. Johnson and D. J. Rowcliffe, "Silicon Nitride Joining," AFOSR Annual Report, Contract No. F49620-81-K0001, March 1983.

[12] I. Idrestedt and C. Brosseit, Acta Chem. Scand. 18[8] 1879-1886 (1964).

[13] R. E. Loehman, "Basic Research on Oxynitride Glasses," Final Report prepared for U.S. Army Research Office, Contract No. DAAG-29-79-C0007, July 1982.

Table I. Major Impurities in Hot Pressed Silicon Nitride[a]

Si_3N_4 Billet	Impurities (wt%)					
	Mg	O	W	Al	Fe	Ca
NC132-I[b]	1.25	2.46	4.0	0.15	0.3	0.03
NC132-II[b]	0.75	2.37	3.5	0.12	0.25	0.12

[a]American Spectrographic Laboratories, San Francisco, CA.
[b]Norton Co. Worcester, MA.

*American Spectrographic Labs, San Francisco, CA.

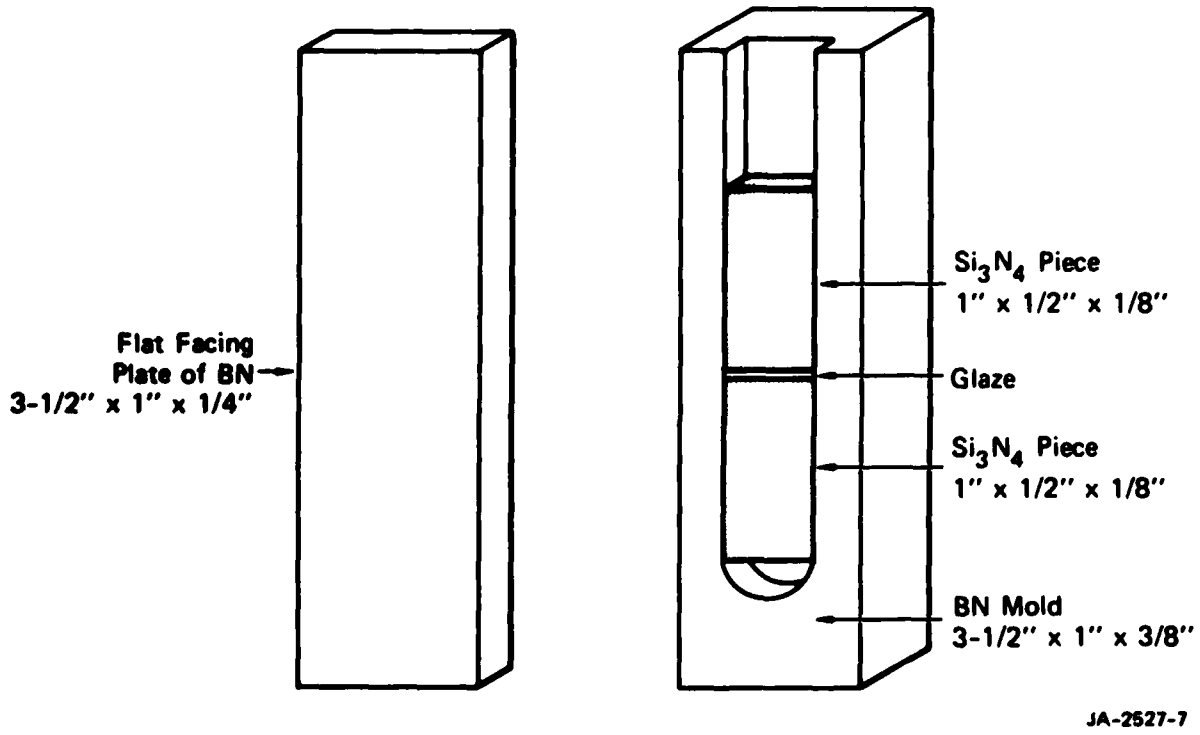

FIGURE 1 BORON NITRIDE JIG USED IN JOINING TWO PIECES OF Si_3N_4

The upper piece is glazed before being joined to the lower piece.

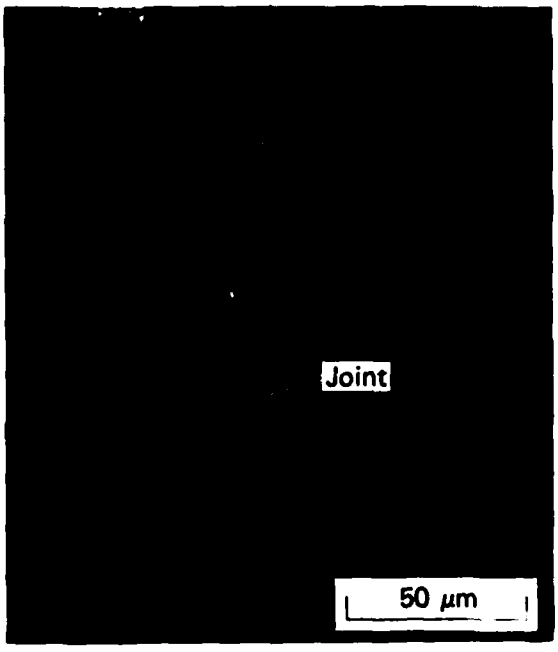

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FIGURE 2 OPTICAL MICROGRAPH OF A THIN JOINT (~5μm)

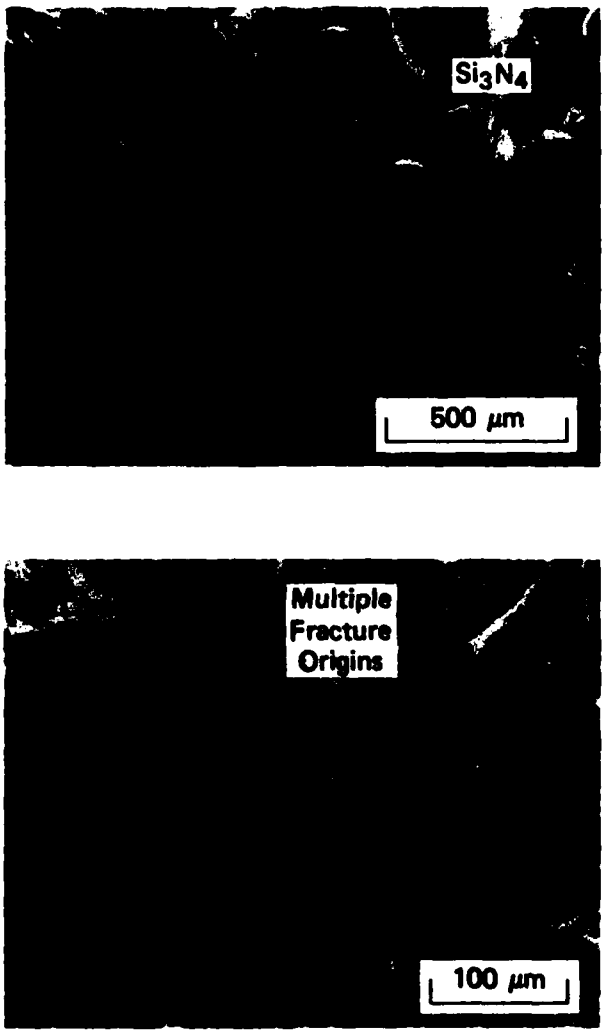

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FIGURE 3 THERMAL EXPANSION CRACKS AND MULTIPLE FRACTURE ORIGINS ON A FRACTURE SURFACE

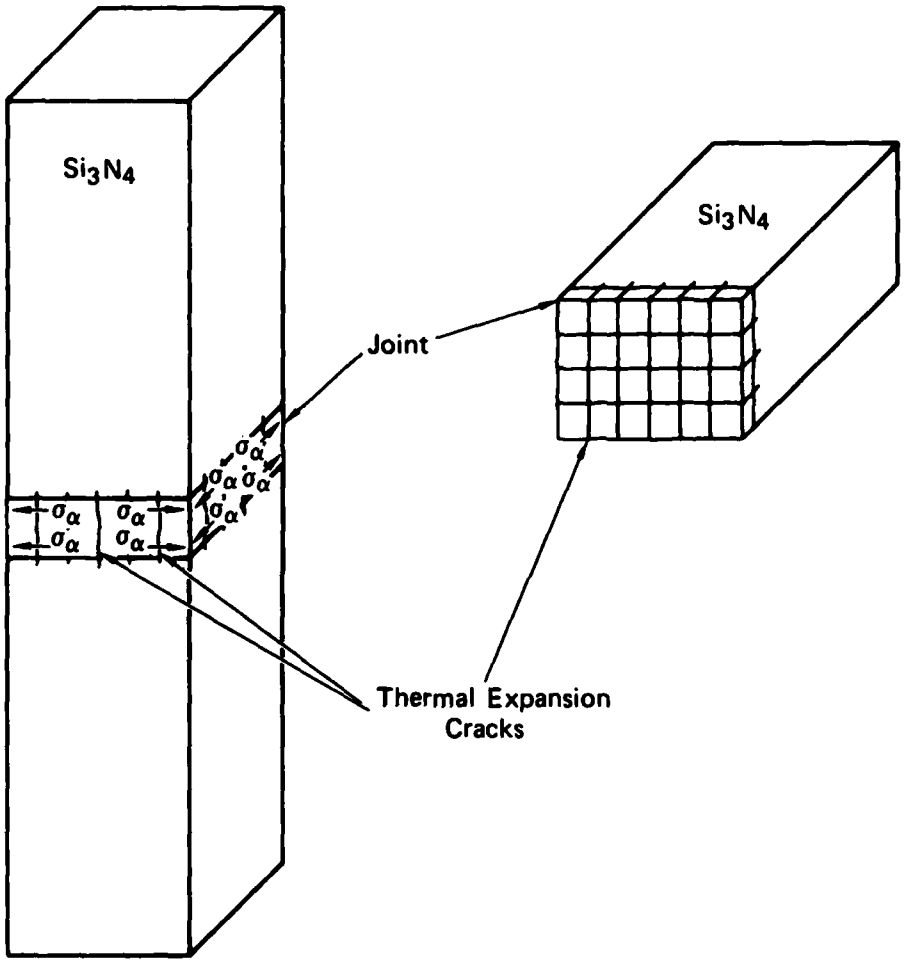

FIGURE 4 SCHEMATIC DRAWING SHOWING DEVELOPMENT OF THERMAL EXPANSION MISMATCH CRACKS IN THE JOINT

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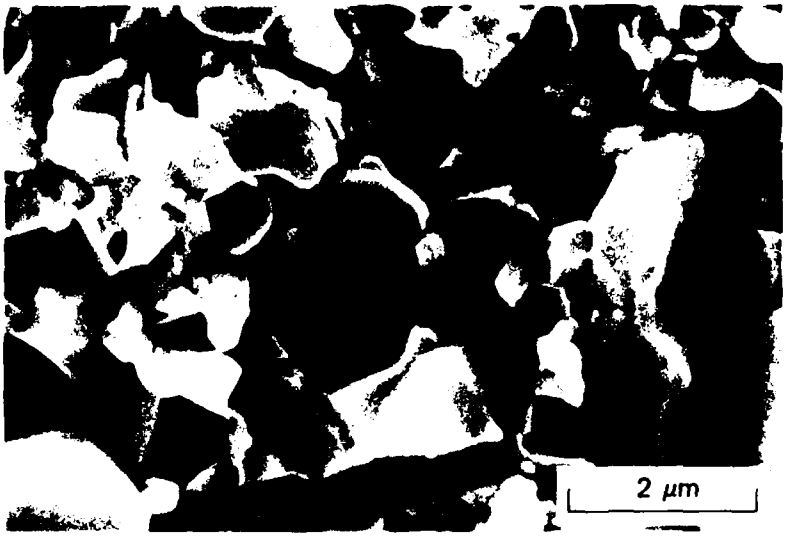
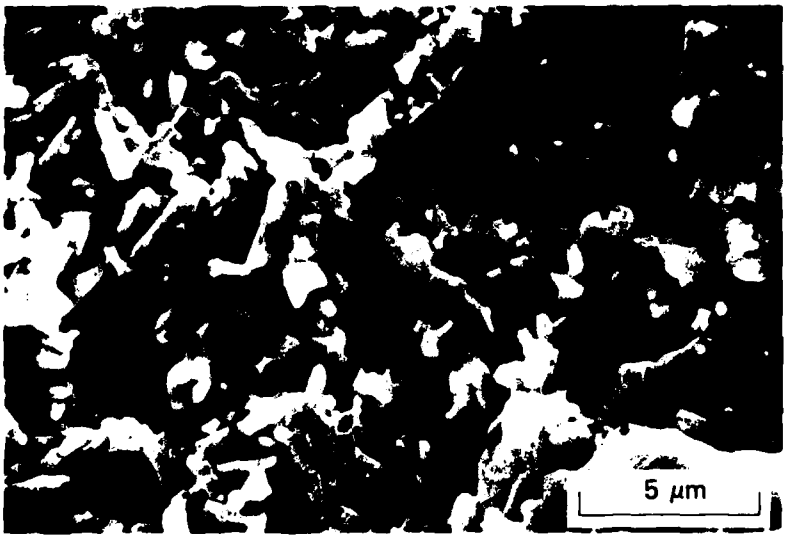
FIGURE 5 TENSILE SURFACE OF A BROKEN BEND BAR SHOWING Si_2N_2O CRYSTALS GROWING INTO THE GLASS



(a) Fracture through Si_3N_4



(b) Fracture through interlocking Si_2N_2O crystals

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FIGURE 6 FRACTURE SURFACES IN A THIN JOINT.

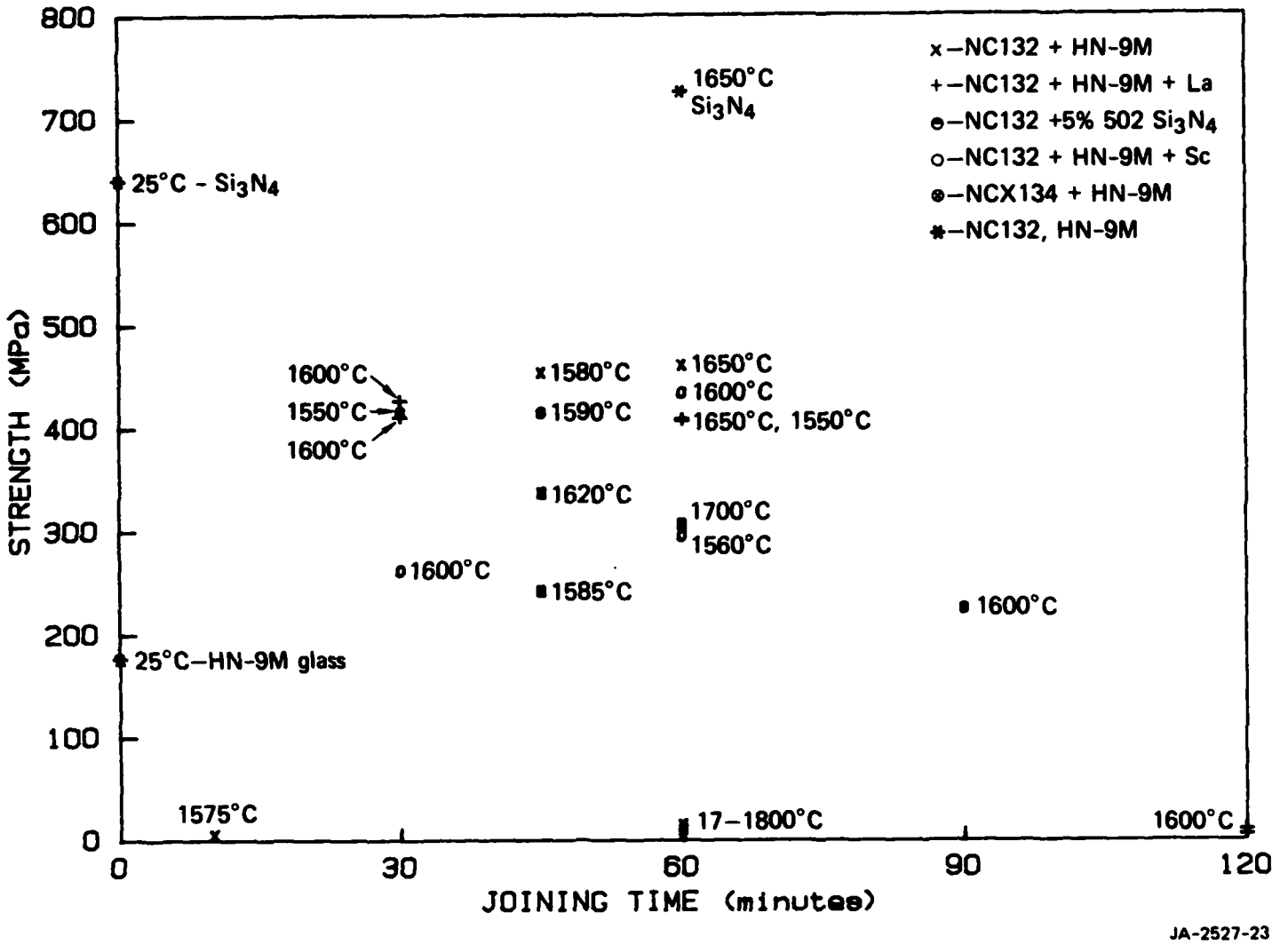


FIGURE 7 MAXIMUM STRENGTHS OF BARS JOINED UNDER VARIOUS CONDITIONS

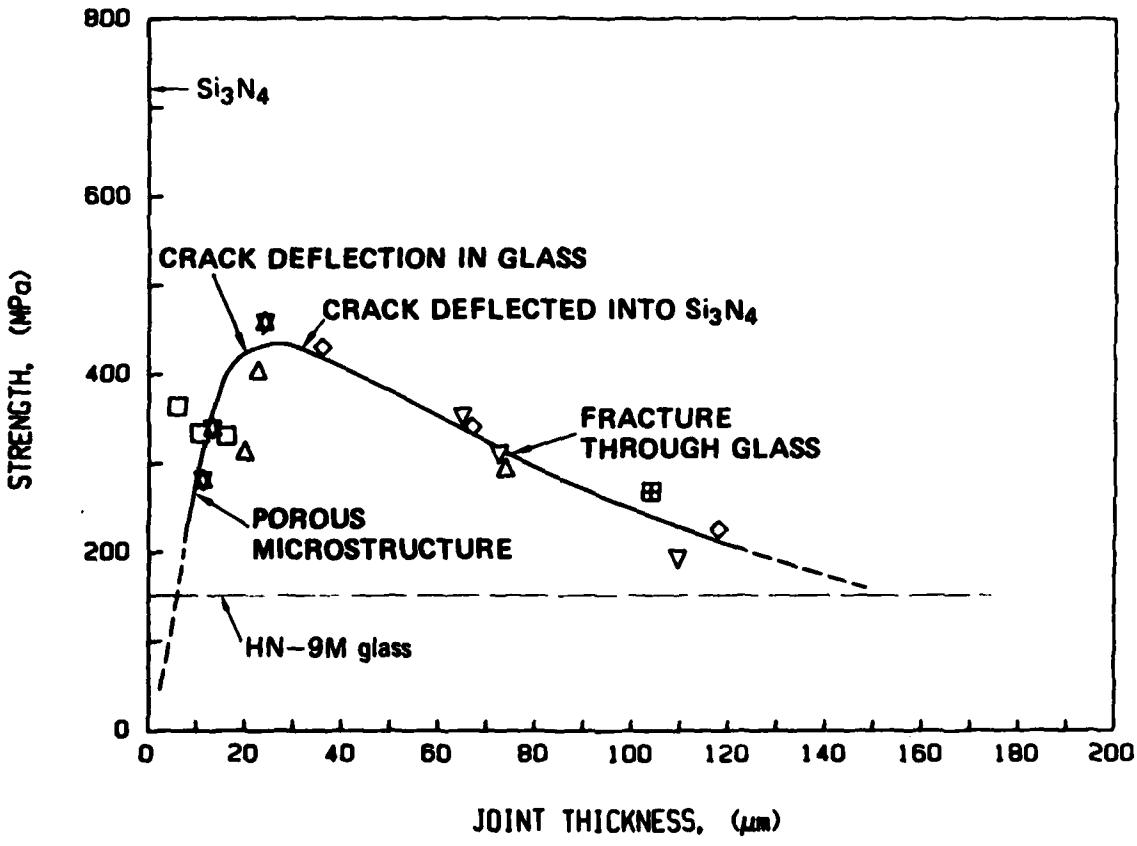
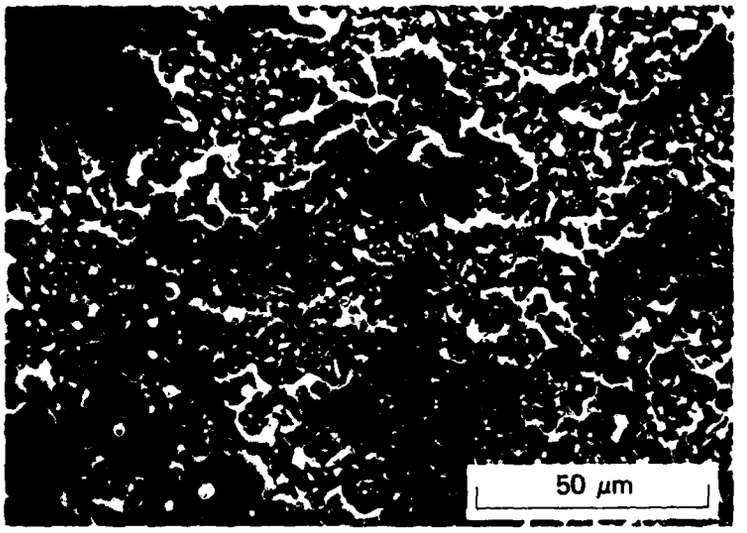
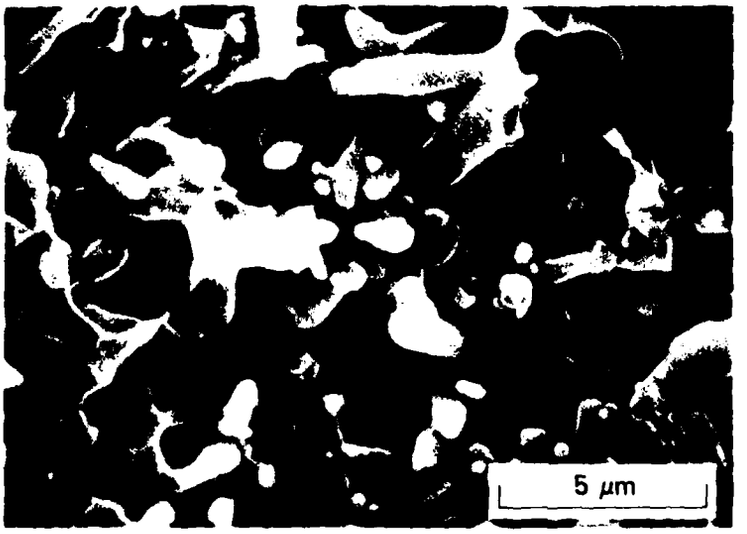


FIGURE 8 STRENGTH VERSUS JOINT THICKNESS

Joining conditions were 1580°C for 45 minutes under 2 atm N_2.
Like symbols indicate test bars cut from a single joined specimen.



(a)



(b)

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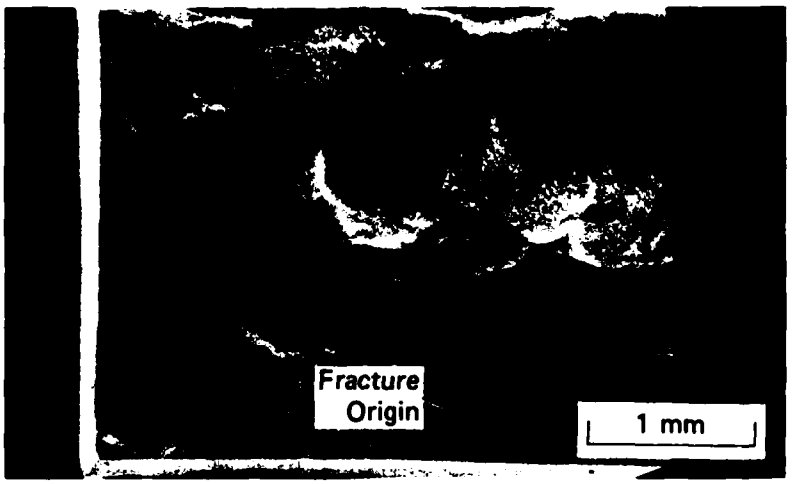
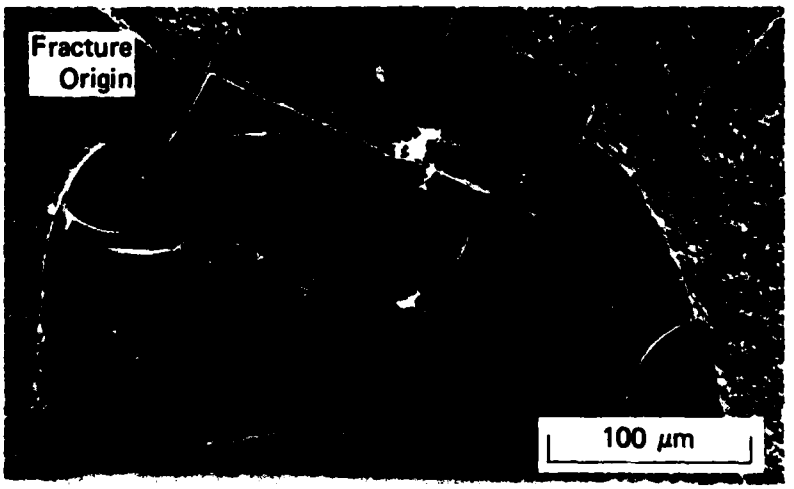
FIGURE 9 MICROSTRUCTURE OF A STRONG THIN JOINT SHOWING (a) DEVELOPMENT OF VOIDS IN JOINT (b) Si_2N_2O CRYSTALS IN GLASS



(a)



(b)

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FIGURE 10 FRACTURE SURFACE SHOWING ORIGIN OF FRACTURE IN GLASS AND SUBSEQUENT FRACTURE PATH THROUGH Si_3N_4

Appendix B

HIGH TEMPERATURE CHEMICAL PHENOMENA AFFECTING SILICON NITRIDE JOINTS*

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Knudsen cell mass spectrometry has been employed to study the chemical processes responsible for joint degradation in joined silicon nitride ceramics. Vapor species present above two commercial hot-pressed silicon nitrides and above three joining glasses have been identified, and partial pressures have been estimated at 1480 K. Oxide vaporization products related to reducing conditions were observed. The implications of these results on proposed silicon nitride joining processes are discussed. It appears that oxygen potential gradients within both glazed and unglazed hot-pressed Si_3N_4 samples are responsible for the enhanced vaporization rates of the sample and the observed instability of glazed joints at high temperatures. Observed vaporization behavior of oxide additives correlates well with that predicted for the chemically reducing environment of Si_3N_4.

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*This work was supported by the Air Force Office of Scientific Research under Contract F49620-81-K-0001.

I. INTRODUCTION

Reliable methods of joining are required before structural ceramics can be used to full advantage in systems such as the various forms of heat engines. Recently, a method of joining Si_3N_4 with an oxide glass was developed[1,2]. The method uses as a joining medium a glass of composition similar to that found as a second phase in hot-pressed or sintered Si_3N_4. Silicon nitride dissolves in the oxide glass that penetrates into the grain boundaries of the bulk material and silicon oxynitride subsequently precipitates as acicular crystals. Ideally, a thin, high strength joint virtually indistinguishable from the bulk material should be formed. This communication describes some aspects of the high temperature behavior, part of an investigation of the chemical and mechanical properties of the system.

The joining method is itself fairly simple. A slurry of powdered glass is applied to one end of a Si_3N_4 piece ~ 2.5 x 1.2 x 0.32 cm. The piece is placed upright in a mold and heated to ~ 1900 K in 200 kPa N_2. The glass forms a thin layer over the end. The glazed piece is then placed above an unglazed piece and heated to ~ 1850-1925 K for 30 to 60 minutes. The joined slab is thus approximately 5 cm long, from which bend bars approximately 5 x 0.32 x 0.32 cm can be cut.

The room temperature strength and microstructure of the joint region are described elsewhere[2]. The strength is independent of the joining conditions, specifically time and temperature, within an optimum range which is 30 to 60 minutes and 1850-1925 K for the NC132 - HN9M system (see Table I for compositions). The strength, however, depends on the joint thickness, with the maximum strength (in four-point-bend)

~ 460 MPa, being achieved with joints ~ 20-30 μm thick. For comparison, the four-point-bend strength of monolithic NC132 is ~ 725 MPa. The joint strengths are far in excess of those previously reported, the best of these being ~ 175 MPa in a system developed by Becher and Halen[3] which uses ZrO_2 as a joining material.

The strength at high temperature is of most interest for demanding structural applications such as advanced gas turbines. Four-point-bend test strengths of Si_3N_4 joined by oxide and oxynitride glasses were measured in air to 1573 K, but were found to be low. Upon heating, the joints expanded considerably and became porous with a consequent loss of strength.

The room temperature strengths of samples that had been heat treated at 1473-1573 K in ~ 200 kPa N_2 to promote crystallization in the joint were considerably lower than those of untreated samples, even though crystallization should have resulted in stronger joints. Examination of fracture surfaces by scanning electron microscopy revealed that the glass was no longer present as a uniform layer over the surface, and in some cases was present only as small islands on the Si_3N_4.

The effects observed after high temperature exposure of the joints, namely joint expansion, joint porosity, and incomplete coverage of the joint area, indicated that chemical processes involving mass transport had occurred. Reactions involving significant amounts of mass transport have been observed for hot-pressed Si_3N_4 and for glasses similar to the grain boundary phases. For example, Cubicciotti and Lau[4,5] reported

transport of magnesium from the ceramic body to the surface in the oxidation of NC132, an MgO-doped Si_3N_4.

Oxynitride glasses volatilize in air at high temperatures, and very high nitrogen pressures are required in their manufacture.[7] The vaporization of gaseous species from Si_3N_4 and oxynitride glasses has not been studied extensively. Lange[8] and Greskovich and Prochazka[9] investigated volatilization of SiO during sintering of Si_3N_4 ceramics, but no experimental studies were done on the vaporization behavior of the glass phase components.

We completed a series of experiments to obtain information on chemical processes occurring in joined Si_3N_4 at high temperature. Knudsen cell mass spectrometry was used to obtain information on vaporization processes relevant to the joint degradation. Vapor species present above glazed Si_3N_4 samples were identified unambiguously by their threshold ionization potentials and isotope abundance patterns, and partial pressures of each species were measured at ~ 1470-1490 K. A glazed Si_3N_4 specimen was sectioned and annealed in nitrogen at high temperature, and then examined by scanning electron microscopy and X-ray microanalysis. The influences of impurities, additives, and reactions between glass and Si_3N_4 upon the mechanical properties of joined silicon nitride have been evaluated in view of known thermodynamic data.

II. EXPERIMENTAL

Knudsen cell mass spectrometry is a direct sampling technique which identifies the gaseous species present above a condensed phase, alone or in the presence of added gases. The sample is loaded into a Knudsen

cell, a cylindrical holder with an orifice which is a very small fraction of the internal surface area of the cell. This low orifice/cell area ratio leads to conditions approaching equilibrium between vapor and condensed phases within the Knudsen cell. The cell is situated in a high vacuum system so that the orifice is in a line-of-sight with the ion source of a mass spectrometer. Gaseous species effuse from the cell in a collision-free molecular beam that essentially freezes chemical composition; species in the beam are then ionized by electron impact, mass analyzed, and detected by the mass spectrometer. The cell is heated by radiation from a tantalum spiral resistance element, and temperatures are measured by optical pyrometry or by means of a thermocouple. A beam-defining slit, which can be moved over the orifice, permits distinction of cell effusate from ambient gases in the vacuum system. The general experimental technique[10,11] and the quadrupole mass filter[12] apparatus used in these experiments have been described previously.

The samples studied in these experiments are described in Table I. The silicon nitride samples are NC132 (1% MgO)* and NCX34 (8% Y_2O_3)*; the indicated oxides were added as sintering aids. The surface area of the bulk silicon nitride samples was 1-2 cm^2. Oxide glasses (HN9M and SG14-0) were prepared by mixing oxide powders (purity >99.5%), melting at 1920 K in air, grinding, and sieving to -100 mesh. The oxynitride

*Norton Co., Worcester, Massachusetts.

glass (SG14) was prepared by adding Si_3N_4 to the oxides; this sample was melted under N_2 at ~ 2000 K before grinding and sieving to -100 mesh.

Each of the separate glasses and silicon nitrides, along with samples of Si_3N_4 which were previously glazed at 1900 K with one of the glass samples in accordance with the established joining procedure, was studied by mass spectrometry. Alumina Knudsen cells with 1.5 mm orifices were heated in air at 1500 K before sample loading to remove volatile impurities. The species over each sample were identified from the respective threshold appearance potentials and isotope abundance patterns of the observed ions. The partial pressures of the vapor species were evaluated at 1470-1490 K by measuring each ion intensity, I^+, at 3 eV above ionization threshold in order to avoid contributions to ion signals by alternative fragmentation processes. The absolute vapor pressure of each species was calculated from the relation

$$P = (kI^+T)/\sigma \qquad (1)$$

where T is the temperature in Kelvins, σ is the relative ionization cross-section, and k is an instrumental sensitivity constant which was evaluated at specific ionizing energies using gold as a vapor pressure standard. Values for σ were taken from the compilation by Mann;[13] additivity of atomic cross-sections was assumed for molecular ions. The mass discrimination observed in quadrupole filters [14] was minimized by adjusting instrument settings to maximize the signal for Au^+ before the calibration run. Instrumental settings were held constant following the gold calibration so that instrument sensitivity would be constant.

Signal intensities at approximately 1470-1490 K were studied as a function of time by measuring the mass spectrum at intervals of 1-3 hours. Following mass spectrometry, the interfacial regions of glazed silicon nitride samples were examined by scanning electron microscopy.

A sample of NC132 glazed with SG-14-0 glass was annealed for 2-3/4 hours at 1100°C in an overpressure of N_2 and subsequently scanned by SEM and X-ray analysis to chart any movement of Mg from the Si_3N_4 into the glass.

III. RESULTS

(1) Mass Spectrometry

Silicon Nitride--A summary of the observed vapor pressures, relative abundances and depletion rates of vapor species above hot-pressed Si_3N_4 samples containing MgO (NC132) and Y_2O_3 (NCX34) at 1480 (± 10)K is presented in Table II. The reported pressures of vapor species must be considered as lower limits of those within each sample. The partial pressures observed in the Knudsen cell will be kinetically limited by (1) low surface areas of grain boundary regions of the silicon nitride surfaces and (2) the viscosity of the molten glasses. The metallic elements observed are present in atomic form, as clearly indicated by threshold appearance potentials. Sodium, potassium, and magnesium were observed during the sample heating at temperatures as low as 1200K. The only non-metallic vapor species were SiO and N_2. We did

not observe Y, Al, W,* or any compounds containing those metals in the vapor above either silicon nitride sample. Vapor pressures of major species decreased much more rapidly above the NCX34 sample; Na, Mg, and SiO decreased 2-4 times faster in the NCX34 than in NC132, although the level of N_2 remained constant in both samples.

Joining Glasses--Partial pressures of major vapor species above each of the joining glasses at 1490 (± 10)K are reported in Table III. In addition to the reported species, Li, Mn, Fe, Ni, Cu, and Se were observed at low signal levels in HN9M. Fe was the only additional species above SG14 glass, while Cu, Ni, and Li were observed at low pressures above SG14-O.

Glazed Silicon Nitride--Levels of major vapor species above four glazed silicon nitride samples at 1480 (± 10)K are given in Table IV. The minor species were the same as those in the component Si_3N_4 and joining glass samples except that N_2 was no longer observed. Initial Na and K pressures were similar in three of the samples, but were much lower in Y_2O_3 hot-pressed Si_3N_4 (NCX34) glazed with an Y_2O_3-containing oxynitride glass (SG14). Both Mg and SiO signal levels were significantly higher in samples containing the oxynitride glass. The SiO levels in the NC132 glazed with SG14 were initially more than a factor of three higher than the levels given in Table IV. During this initial phase, "bursts" in the SiO^+ signal were observed; the signal was observed repeatedly to increase sharply before settling back to a stable

*Tungsten-containing particles present in the Si_3N_4 result from WC ball milling and thus tungsten vaporization was of interest.

intermediate level. Signals of other species were stable, and no instability in SiO^+ signal was observed in other glazed Si_3N_4 samples. Although a careful comparison of depletion rates of vapor species in each sample was not undertaken, we did observe gradual depletion of all vapor species in each sample, with the exception that SiO evolution above samples glazed with SG14 was almost constant after 1-2 hours.

Microscopy--Figures 1 and 2 show the glazed region of NC132/HN9M and NC132/SG14, respectively, before and after the mass spectrometric measurements. The latter sample exhibited the worst degradation. The glass layers on glazed samples are initially dense and smooth, with the only defects being thermal expansion cracks normal to the interface. After the measurements, the layers were very porous and extensively cracked. The SG14 layer (Fig. 2b) shows the most damage and contains many "bubbles". The large bubbles are most likely due to the decomposition of the oxynitride glass in the vacuum conditions of the mass spectrometer. Figure 2c shows the region close to the interface in the NC132/SG14 sample. The acicular crystals are Si_2N_2O,[1] and indicate that, although the glass is damaged, the interface is itself intact. These crystals of Si_2N_2O, which have been observed in other Si_3N_4/glass systems, are more distinct in NC132/SG14 after the mass spectrometric studies.

(2) Annealed Specimens

An X-ray microanalysis scan across the interface of an annealed NC132/SG14-0 sample revealed Mg in the glass at distances of up to 60 μm from the interface. As Mg was not originally present in the

glass, this observation indicates that Mg has diffused from the Si_3N_4 into the glass. The composition changes at the interface and in the glass are complex and will be the subject of a future paper.[15]

IV. DISCUSSION

The present study investigated various phenomena affecting Si_3N_4 joints at high temperature. Although the separate observations appear to indicate that the chemistry involved is complex, the results are consistent with the general pattern of Si_3N_4 ceramic chemistry that involves equilibria, kinetic factors, oxidation-reduction processes, and silicate solution properties.

Joint degradation at high temperature was characterized by expansion, porosity, and areas from which the joining glass had disappeared; these effects imply that material was being transported to or from the joints. Chemical activity gradients are the driving force for mass transport; a given substance will tend to move toward a region in which it has lower activity. Chemical activity was defined by G. N. Lewis as the ratio of the fugacity of a component to its fugacity in a standard state; for a gaseous component, the fugacity is equal to its partial pressure corrected for gas nonideality.[16] Knowledge of the pressures of gaseous species in equilibrium with condensed phases of different compositions thus enables the prediction of the direction of mass transport, irrespective of whether a condensed phase or gas phase mechanism is involved.

The compounds encountered in the Si-O-N system are Si_3N_4, Si_2N_2O, and SiO_2. Silicon nitride exposed to relatively high oxygen potentials

develops a surface layer of silica with at most a thin intermediate layer containing silicon oxynitride; exposure at low oxygen pressures produces volatile SiO as a reaction product. In terms of oxidation-reduction chemistry, the bulk of a silicon nitride body, including intergranular phases resulting from use of oxide sintering aids, is a reducing environment when compared to the intermediate oxynitride-rich region and the relatively oxidizing surface silicate phase.

Chemical conditions within the ceramic are dominated by the reducing properties of Si_3N_4, which affect the stability of oxide materials in the intergranular phase. The enhanced vaporization of oxide materials under reducing conditions is well known; MgO, for instance, becomes an unsuitable refractory material because of the evolution of atomic Mg. The chemical activities of oxide components, which are closely related to their vapor pressures, will be higher within Si_3N_4 ceramics than under the more neutral or oxidizing conditions found at exposed surfaces of interfaces with glasses of higher oxygen potential. These chemical activity gradients provide a driving force for material transport leading to joint degradation, as well as for phenomena such as the MgO transport observed by Cubicciotti and Lau[4] for NC132 oxidation. It should be noted that this driving force is in addition to the tendency of components of silicate solutions to achieve uniform distributions under conditions of constant oxygen potential.

Figure 3 shows the partial pressures of principal vaporization species of pure Na_2O, MgO, SiO_2, Al_2O_3, and Y_2O_3 at 1480 K calculated from thermodynamic data[17,18] as a function of oxygen potential. The

pressures increase as the oxygen potential decreases. Similar plots could be made for other oxides. For a given oxygen potential, Na_2O is more volatile, and Al_2O_3 and Y_2O_3 are less volatile, than SiO_2 and MgO, which have similar volatilities. In the ceramics, silicate solution effects will lower component activities to some extent, but the general trends will remain the same.

The results of the present study are in excellent agreement with the implications of Figure 3. As seen in Table II, Mg, SiO, and Na are the major vaporization species evolved from both NC132 and NCX34; Mg in NCX34 is notable since it is an impurity rather than an intended constituent. The observed Mg pressure over both ceramic grades is two to three orders of magnitude greater than for congruent vaporization of MgO under neutral conditions. The Na pressure is less than that expected for neutral vaporization, but Na is present as an impurity stabilized in silicate solution in low concentration. In accord with the low volatilities of Al and Y oxides, neither Al nor Y vapor species were observed.

On the basis of concentration and volatility considerations, the SiO, Mg, Na, and K pressures measured over the Y oxynitride glass (SG14) should have been greater than those measured over the Y oxide glass (SG14-O) because of the lower oxygen potential of the oxynitride. This was true for SiO and Mg, but not for Na and K. In all likelihood, significant portions of the small amounts of Na and K initially present as impurities were lost during the preparation of the oxynitride glass. The higher pressures seen for Mg and Na in the magnesia-doped glass (HN9M) probably reflect their greater concentration in these

specimens. The lowest Na and K were observed over NCX34 glazed with SG14 (Table IV), probably reflecting lower amounts in the ceramic and glass. However, the SiO and Mg observed over both NC132 and NCX34 were greater for the oxynitride-glazed specimens, in accord with their lower oxygen potential.

The observation of extensive vaporization of Mg in joints and in commercial grades of Si_3N_4 has other implications. Our results are consistent with the reaction:

$$Si_3N_4(s) + 3MgO(s) = 3SiO(g) + 3Mg(g) + 2N_2(g).$$

This behavior explains the relative difficulty of sintering Si_3N_4-MgO powder compacts to high density at atmospheric pressure[19], compared to hot pressing in which vaporization is suppressed or to pressureless sintering in the Si_3N_4 - Y_2O_3 - Al_2O_3 system.

V. CONCLUSIONS

The presence of chemical gradients related to oxygen potentials has significant consequences for Si_3N_4 joining technology. Considerable chemical transport must be expected for intergranular phase substances if significant chemical activity gradients are present when an oxide glass is used as a joining material. This is in accord with the expansion observed at high temperature for existing joints. Material loss from the joint by vaporization of SiO, Mg, and other volatile species is also expected. Alkali and alkaline earth metal oxide impurities should be minimized in Si_3N_4 ceramics, since they will rapidly transport to joints made with oxide glasses.

Joining of MgO hot-pressed silicon nitride with oxide glasses appears to be impractical for high temperature use. On the basis of the lower rates of transport observed in oxidation experiments,[5] joints made with Al_2O_3 and Y_2O_3 hot-pressed Si_3N_4 ceramics should have somewhat better high-temperature performance than that observed for the MgO hot-pressed material. Fabrication of Si_3N_4 joints with stable high temperature properties will require the elimination of additive concentration and oxidation potential gradients at the joint.

References

[1]R. E. Loehman, M. L. Mecartney, and D. J. Rowcliffe, "Silicon Nitride Joining", Annual Report, AFOSR, Contract F49620-81-K-0001, February 1982.

[2]S. M. Johnson and D. J. Rowcliffe, "Silicon Nitride Joining", Annual Report, AFOSR, Contract F49620-81-K-0001, March 1983.

[3]P. F. Becher and S. A. Halen, "Solid State Bonding of Si_3N_4," Am. Ceram. Soc. Bull. 58 [6] 582-583 (1979).

[4]D. D. Cubicciotti and K. H. Lau, "Kinetics of Oxidation of Hot-Pressed Silicon Nitride Containing Magnesia," J. Am. Ceram. Soc., 61 [11-12] 512-517 (1978).

[5]D. D. Cubicciotti and K. H. Lau, "Kinetics of Oxidation of Yttria Hot-Pressed Silicon Nitride," J. Electrochem. Soc., 126 [10] 1723-1728 (1979).

[6]D. D. Cubicciotti, R. L. Jones and K. H. Lau, "High Temperature Oxidation and Mechanical Properties of Silicon Nitride," Interim Report, AFOSR Contract F44620-76-0116, November 1977.

[7]R. E. Loehman, "Basic Research on Oxynitride Glasses," U. S. Army Research Office, Contract DAAG-29-79-C-007, July 1982.

[8]F. F. Lange, "Volatilization Associated with the Sintering of Polyphase Si_3N_4 Materials," J. Am. Ceram. Soc. 65 [8] C-120-C-121 (1982).

[9]C. Greskovich and S. Prochazka, "Stability of Si_3N_4 and Liquid Phases During Sintering," J. Am. Ceram. Soc.64 [7] C-96-C-97 (1981).

[10]D. L. Hildenbrand, "Mass Spectrometric Studies of Bonding in the Group IIA Fluorides," J. Chem. Phys. 48 [8] 3657-3665.

[11]D. L. Hildenbrand, "Dissociation Energies and Chemical Bonding in Alkaline-Earth Chlorides from Mass Spectrometric Studies," J. Chem. Phys. 52 [11] 5751-5759 (1970).

[12]R. D. Brittain and D. L. Hildenbrand, "Catalytic Decomposition of Gaseous SO_3," J. Phys. Chem. 87 [19] 3713-3717 (1983).

[13]J. B. Mann, "Ionization Cross Sections of the Elements Calculated from Mean-Square Radii of Atomic Orbitals," J. Chem. Phys. 46 [5] 1646-1651 (1967).

[14]T. C. Ehlert, "Determination of Transmission Characteristics in Mass Filters," J. Phys. E. 3, 237 (1970).

[15]S. M. Johnson, R. D. Brittain, R. H. Lamoreaux, and D. J. Rowcliffe, "Cation Transport in Si_3N_4/Glass Couples," to be submitted to J. Am. Ceram. Soc.

[16]G. N. Lewis and M. Randall, Thermodynamics, 2nd ed., K. S. Litzer and L. Brewer, Eds. McGraw-Hill, New York, 1961.

[17]D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., NSRDS-NOS37, U.S. Government Printing Office, Washington, DC, 1971, and supplements.

[18]V. P. Glushko, L. V. Gurvich, et al., "Thermodynamic Data for Individual Substances," Vol. 4, Institute for High Temperatures, National Academy of Sciences of the U.S.S.R., Moscow, 1983.

[19]G. R. Terwilliger and F. F. Lange, "Pressureless Sintering of Si_3N_4," J. Mater. Sci. 10 [7] 1169-1174 (1975).

Table I. Samples Investigated by Mass Spectrometry

Sample	Designation	Nominal Composition (wt %)				
		Mg	Y	W	Al	Fe
MgO Hot-Pressed Si_3N_4	NC132	0.8	---	1.8	0.2	0.2
Y_2O_3 Hot-Pressed Si_3N_4	NCX34	---	5.3	2.1	0.2	0.3
		MgO	SiO_2	Al_2O_3	Y_2O_3	N
MgO Glass	HN9M	35	55	10	---	---
Y_2O_3 Glass	SG14-0	---	34	20	46	---
Y_2O_3 Oxynitride Glass	SG14	---	32	19	43	6

Table II. Partial Pressures, Relative Abundances, and Depletion Rates of Vapor Species Above Si_3N_4 Samples at 1480 K

Vapor Species	Relative Abundance		Pressure (mPa)		Depletion Rate (%/h)	
	NC132	NCX34	NC132	NCX34	NC132	NCX34
SiO	100.0	100.0	317	528	14	43
Mg	100.7	15.9	324	84	13	60
Na	193	10.4	627	55	24	40
K	12.2	1.1	40	6	27	57
N_2	4.1	12.5	13	66	0	0
Mn	8.2	2.7	27	14	20	59
Fe	2.8	0.7	9	4	19	45
Li	0.4	0.3	1.4	1.4	40	33
Ni	0.2	0.3	0.7	1.5	40	0
Se	---[a]	0.3	---	1.6	---	0
Y	---	---	---	---	---	---
Al	---	---	---	---	---	---
W	---	---	---	---	---	---

[a] --- indicates Not Detected

Table III. Partial Pressures of Major Vapor Species above Joining Glasses at ~ 1490 K

Vapor Species	Partial Pressure (mPa)		
	HN9M	SG14	SG14-O
SiO	99	334	1.3
Mg	8.8	3.7	1.5
Na	331	5.6	76
K	9.3	0.6	7.8

Table IV. Partial Pressures Above Glazed Si_3N_4 Samples at ~ 1480 K

Vapor Species	Partial Pressure (mPa) NC132+NH9M	NC132+SG14	NCX34+SG14	NCX34+SG14-O
SiO	25	132	58	6.5
Mg	11	48	14	3.2
Na	72	66	13	73
K	1.9	1.9	<0.5	1.9

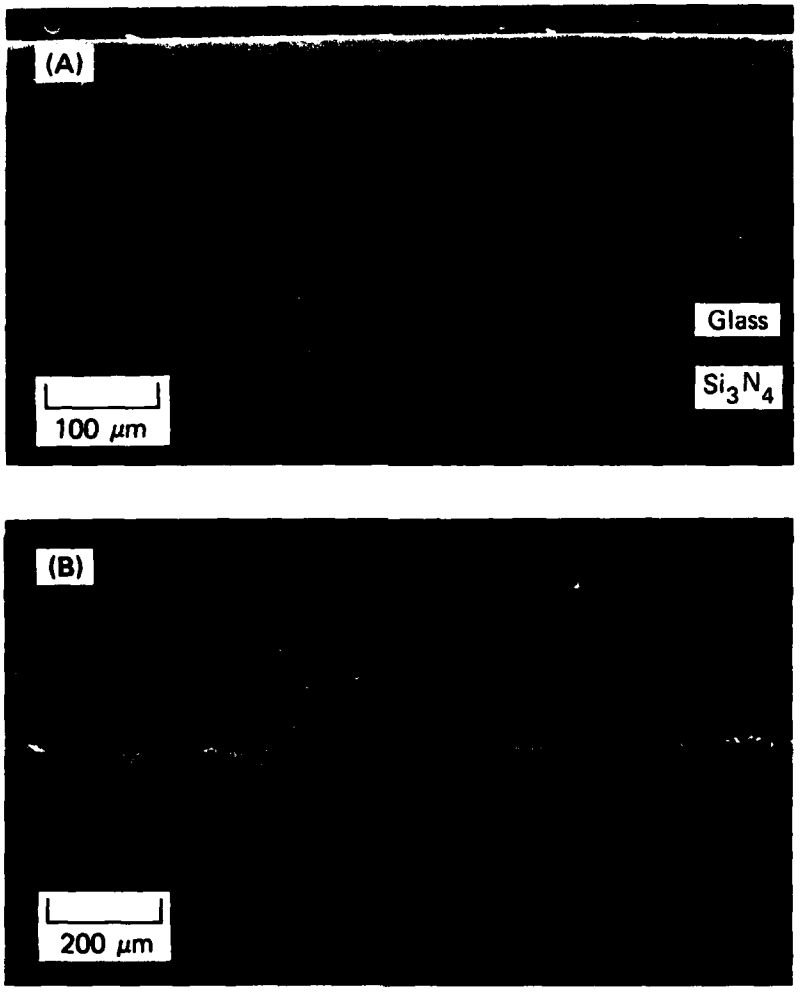

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FIGURE 1 NC-132 (MgO) Si_3N_4 GLAZED WITH MAGNESIA (HN-9M) GLASS

(A) As glazed.
(B) After heating to 1480 K in mass spectrometer.

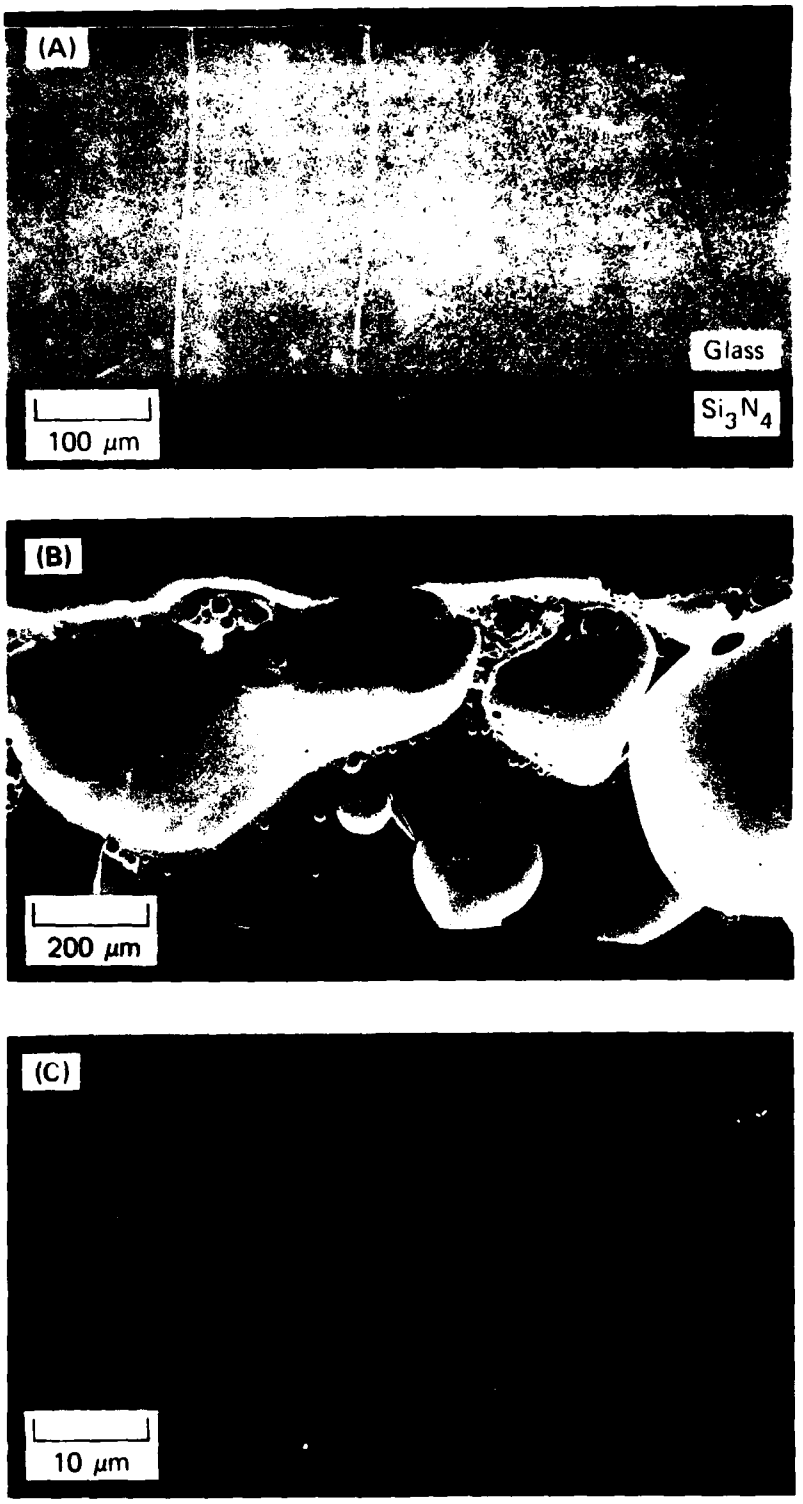

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FIGURE 2 NC-132 (MgO) Si_3N_4 GLAZED WITH YTTRIUM OXYNITRIDE GLASS (SG-14)

(A) As glazed.
(B) After heating to 1480 K in mass spectrometer.
(C) Interfacial region of (B) showing Si_2N_2O crystals.

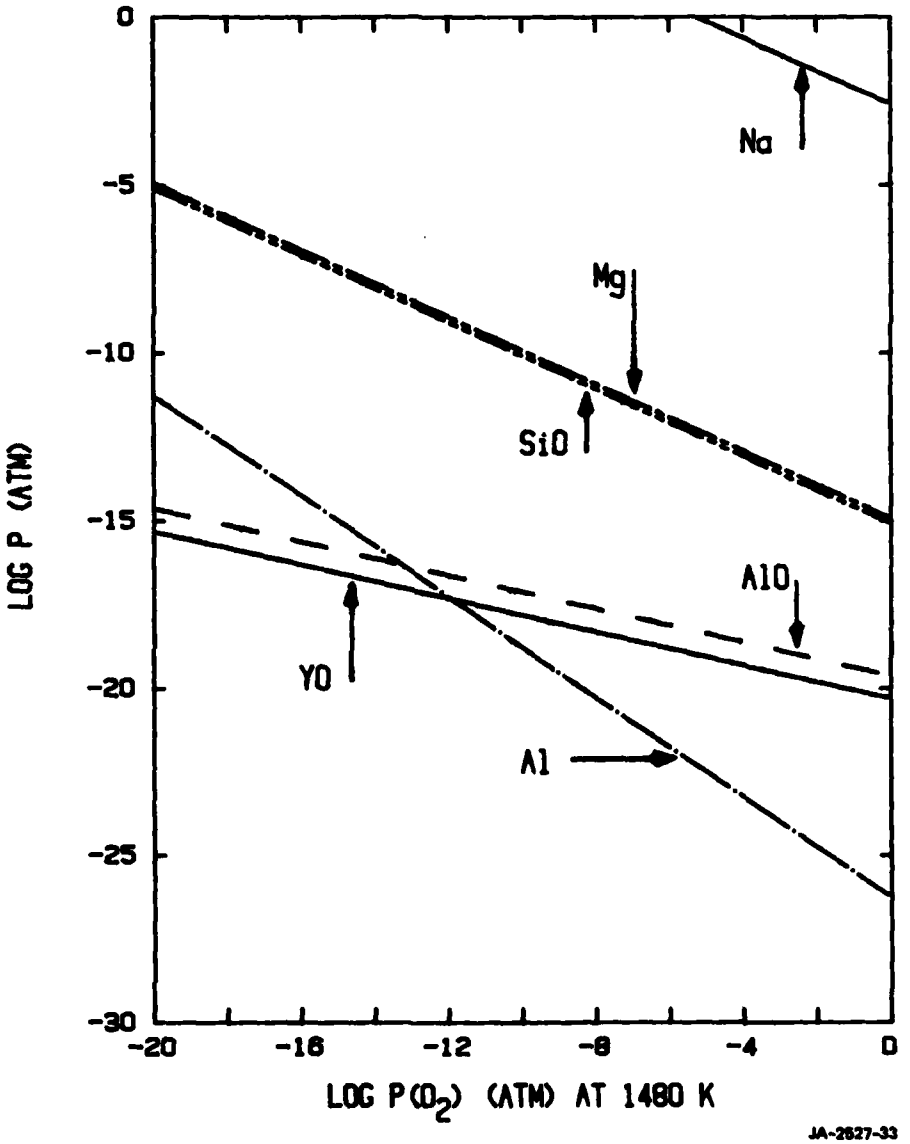

FIGURE 3 PRESSURES OF PREDOMINANT VAPORIZATION SPECIES OF PURE Na_2O, MgO, SiO_2, Al_2O_3 AND Y_2O_3 AS FUNCTIONS OF OXYGEN POTENTIAL AT 1480 K

Appendix C

SUMMARY OF WORK COMPLETED

RESEARCH ON SILICON NITRIDE JOINING

Stanford Subcontract #SRI C-10383

R. Sinclair, P.I.

This report summarizes the work done by M. L. Mecartney on the Si_3N_4 joining project during the period of December 1, 1980 through November 30, 1983. A complete description is in preparation and is to be submitted as a Ph.D. thesis for Stanford University. Results from five main areas of the research are presented. These topics include:

1. Comparison of the glass composition used for joining with the grain boundary phase in hot-pressed Si_3N_4.

2. Si_3N_4/glass reactions in melts.

3. The microstructure and mechanical properties of joined Si_3N_4.

4. The effect of dissolved Si_3N_4 on the properties of the joining glass.

5. Crystallization behavior.

GLASS COMPOSITION

The composition of glass (HN-9M) used to join Si_3N_4 was 10 wt. % Al_2O_3 35 wt. % MgO, 55 wt. % SiO_2. This composition was compared to the grain boundary composition of the host NC132 Si_3N_4 by two methods. Firstly, an average grain boundary composition was calculated based on cation and oxygen analyses of a bulk piece of NC132 Si_3N_4 (using the same procedure as Loehman had used for the powder lots). The second technique employed was energy dispersive spectroscopy (EDS) in transmission electron microscopy (TEM) to analyze pockets of glass in the NC132 Si_3N_4. The two results are shown on the MgO-Al_2O_3-SiO_2 ternary phase diagram of Fig. 1. The NC132 used in these experiments was most likely made from the powder lot HN-10 since those compositions most closely matched. The lower Al content in the EDS analysis may be due to some small Al solubility in the Si_3N_4. The higher Si content could be from Si_3N_4 dissolved in the glass. The HN-9M glass was a reasonable match for the grain boundary phase without nitrogen.

The elastic modulus of the glass, measured using an acoustic resonance technique, was 140GPa.

Si_3N_4Glass Melts

Loehman's work on analyzing the phase reactions of amorphous and α-Si_3N_4/glass melts was continued using β-Si_3N_4 powders. The powder x-ray diffraction (XRD) results showed that the rate of dissolution for 15 wt. % Si_3N_4 in 85% glass were slowest for β-Si_3N. Si_2N_2O appeared as an intermediate phase for the melts with both high and low concentration of Si_3N_4. TEM analysis showed lath-like Si_2N_2O precipitates near dissolving Si_3N_4 particles (Fig. 2). The Si_3N_4 was inhomogeneously distributed.

It is postulated that the following reactions occurred during the heating of the melts at 1650°C and caused the amount of Si_2N_2O to decrease, despite the two atmospheres nitrogen pressure used.

$$Si_3N_4(s) + SiO_2(l) \longrightarrow 2Si_2N_2O(s) \quad (1)$$

$$Si_2N_2O(s) + SiO_2(l) \longrightarrow 3SiO(g) + N_2(g) \quad (2)$$

The maximum solubility of Si_3N_4 in the HN-9M glass was 12 - 15 wt. %. A minimum amount (2.5 wt. % Si_3N_4) was needed in order to prevent devitrification of the glass into $MgSiO_3$, when cooled in a graphite element furnace at a rate of 44°C/minute.

Joined Si_3N_4

Four point bend tests were conducted on joined samples, the NC132 Si_3N_4, and the HN-9M glass (Results are presented in Fig. 18 of the March 1983 Annual Report). The strengths of the joined samples fell half-way between the strength of the Si_3N_4 and that of the glass. The strengths did not appear to be correlated to joining times (for 20 min. $< t <$ 120 min) or joining temperature (1550°C $< T <$ 1700°C). Scanning electron microscopy (SEM) was performed on the samples and showed that the fracture path went through both the Si_3N_4 and the glass. It also indicated the presence of extensive cracks perpendicular to the interface which were probably caused by the thermal expansion mismatch between the glass and the Si_3N_4.

TEM of the joined samples showed that Si_2N_2O had precipitated out at the interface where the Si_3N_4 had dissolved away. The original presence of Si_3N_4 was confirmed by the remaining W-Fe rich impurity particles, which act as markers of the original interface (Fig. 11 in February 1982 Annual Report).

5 wt. % α-Si_3N_4 had been added to the joining glass for some experiments, in order to promote the precipitation of Si_2N_2O. The strengths of these samples were average. Since the solubility of Si_3N_4 glass is 15 wt. %, this amount is probably too small to cause extensive reactions. TEM analyses did show increased Si_2N_2O precipitation near the interface in the glass (Fig. 3). Few W-Fe particles can be seen and so this region was not originally NC132 Si_3N_4. The Si_2N_2O particles did not extend across the interface. Enlarged pockets of glass were found in the Si_3N_4 near the interface for all joined samples (Fig. 4). Sc_2O_3 and La_2O_3 were added to some joining glass for some experiments and used as tracers to determine how far into the Si_3N_4 the joining glass diffused. EDS with SEM was tried first but was unsuccessful due to the small concentrations of Sc and La. TEM with EDS analysed discrete pocketsof glass and traces of Sc were found as far in as 700 μm (Fig. 8 of March 1983 Annual Report). This gives an approximate diffusion coefficient of $D = 10^{-6} cm^2/sec$ at 1600°C.

Microindentation was used to correlate the change in microstructure with local changes in mechanical properties. Figures 5 and 6 show that there is a sharp drop in hardness and fracture toughness for the Si_3N_4 near the interface (closer than 100μm). This region corresponds to the areas where large amounts of glass had been discovered by TEM. The smaller enlarged pockets at distances greater than 100μm into the Si_3N_4 did not degrade the room temperature hardness or fracture toughness.

Effect of Dissolved Si_3N_4 on the Properties of HN-9M Glass

Samples of HN-9M glass and various amounts of Si_3N_4 were melted at 1650°C for one hour in a nitrogen atmosphere. As mentioned previously if $\geq$2.5% Si_3N_4 was added, crystallization was inhibited. Lesser amounts of Si_3N_4 allowed $MgSiO_3$ to precipitate. Samples with 2.5 to 15 wt. % Si_3N_4

were sent out for determination of the nitrogen concentration by gas fusion reaction. These results, which can err on the low side, indicated that only half of the nitrogen from the dissolved Si_3N_4 had remained in the glass. These samples were then used for indentation tests to ascertain the variation in hardness and elastic modulus with nitrogen content. Figures 7 and 8 present the data showing an increase in hardness and modulus with increasing nitrogen concentration. These results agree well with the work on other oxynitride glass systems, which suggest that the nitrogen leads to increased cross linking and a tighter bound glass structure and hence the increase in hardness and modulus [1].

R. E. Loehman of Sandia Labs provided glass transition temperature and thermal expansion measurements. The thermal expansion measurements did not show any systematic decrease with increasing nitrogen content while the glass transition temperature increased from 750°C at 0 at. % N to 850°C at 4 at. % N.

Combining the hardness vs nitrogen concentration data with information about the average hardness of the glass in the joints (found by microindentation), provided a method for determining the nitrogen content of the glass in the joint. According to Figure 7, the nitrogen content was about 4 at. % This nitrogen concentration is within the range of that found by Clarke and Zaluzec in the grain boundary phase of hot-pressed Si_3N_4 by using electron energy loss spectroscopy [2]. This is also at the limit of saturation for Si_3N_4 in the glass. Chemically, the glass joint indeed did resemble a large angle grain boundary.

Crystallization

Si_3N_4/glass melts with Si_3N_4 concentrations from 5-15% were heat treated at 1300°C for times from 0.5 hours to 2 hours. The results

(Fig. 18 in March 1983 Annual Report) showed predominently $MgSiO_3$ precipitating. The higher was the Si_3N_4 content, the longer the sample took to crystallize.

TEM of joined samples heat treated at 1300°C showed strained particles of $MgSiO_3$ and occasionally Mg_2SiO_4 (Fig. 9). The strain, indicated by the distorted bend contours, was due to the difference in thermal expansion coefficient and change in density between the glass and the crystalline phases. The pockets of glass were high in Al and Ca (Fig 19 March 1983 Annual Report).

The Sc-HN-9M glass used for the tracer experiments had spontaneously crystallized in certain regions (Fig 10). The crystallites were fine particles which 2 ½ D imaging in TEM showed to be close in orientation. Segregation of pockets of glass was not observed, and the crystallized regions had the same Sc-Mg-Al-Si composition as the original glass.

REFERENCES

1. R. E. Loehman "Oxynitride Glasses", J. of Non Cryst. Solids 42, 433-446 (1980).

2. D. R. Clarke, N. J. Zaluzec "The Intergranular Phase in Hot-Pressed Silicon Nitride: III, A Refinement of the Elemental Composition", J. Am. Cer. Soc. 65 (8) C-132-133 (1982).

FIGURE CAPTIONS

FIGURE 1 $MgO-Al_2O_3-SiO_2$ Phase Diagram
HN-9 and HN-10 are calculated grain boundary phases for two powder lots of NC132 Si_3N_4. HN-9M is the base composition used for joining. NC132 is the calculated grain boundary phase from the bulk Si_3N_4. EDS is the composition obtained by EDS analyses in TEM of glassy pockets in NC132.

FIGURE 2 Si_2N_2O precipitating near a dissolving β-Si_3N_4 grain in a Si_3N_4/glass melt with 15% Si_3N_4 and 85% glass.

FIGURE 3 Si_2N_2O precipitates in the glass of a joined sample. 5 wt. % α-Si_3N_4 had been added to the glass.

FIGURE 4 Si_3N_4 grains surrounded by glass 10 μm away from the interface. The amorphous regions are marked by g.

FIGURE 5 Variation in hardness as a function of distance into the Si_3N_4 away from the Si_3N_4/glass interface.

FIGURE 6 Variation in fracture toughness as a function of distance into the Si_3N_4 away from the Si_3N_4/glass interface.

FIGURE 7 Variation in hardness with nitrogen content for HN-9M glass.

FIGURE 8 Variation in elastic modulus with nitrogen content for HN-9M glass .

FIGURE 9 $MgSiO_3$ precipitate (indicated by Mg) in the Si_3N_4 close to the joint interface. The residual glass high in Al and Ca is marked by G.

FIGURE 10 Dark field image of a crystallized Sc-Mg-Al-Si phase.

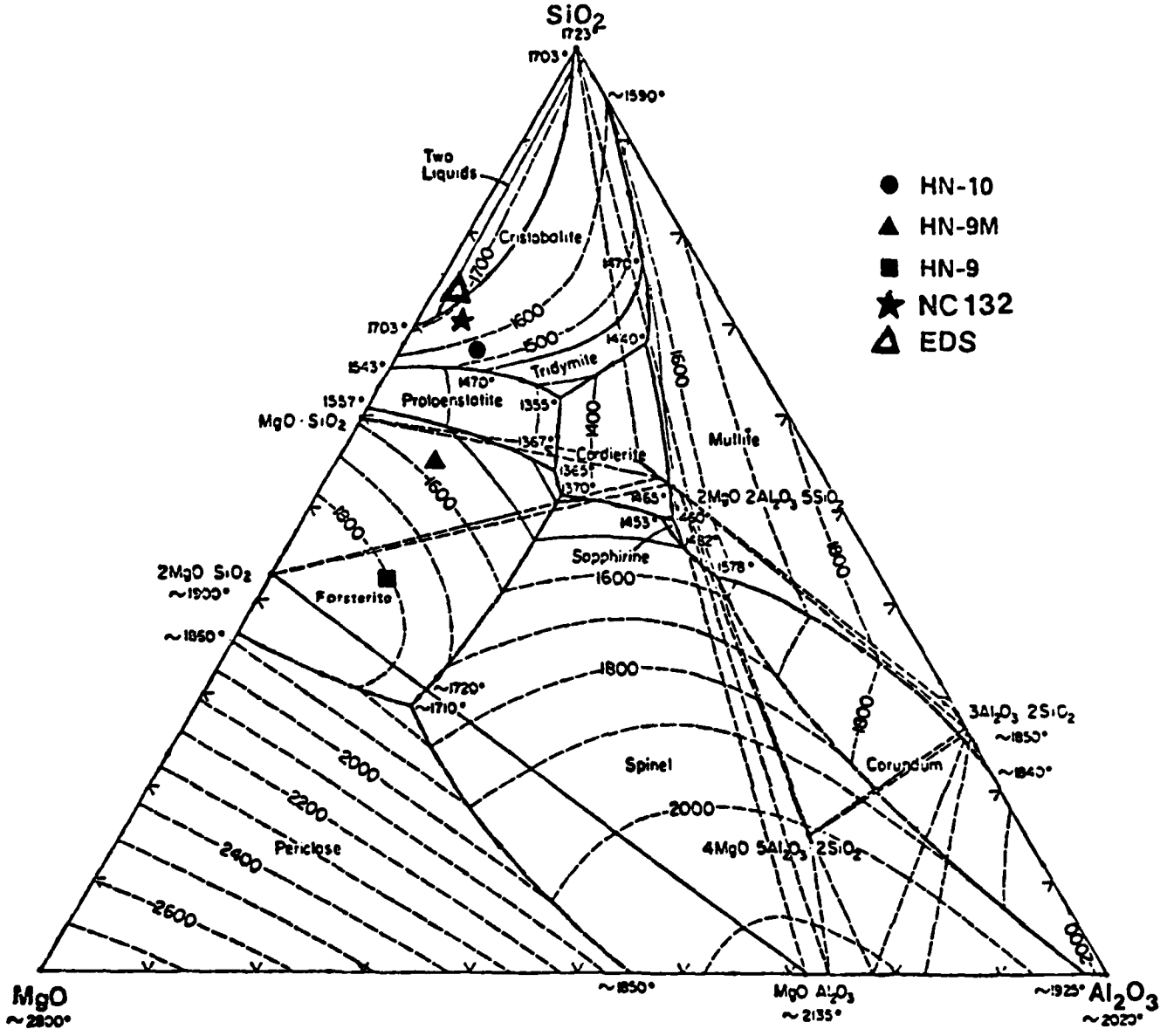

FIGURE 1

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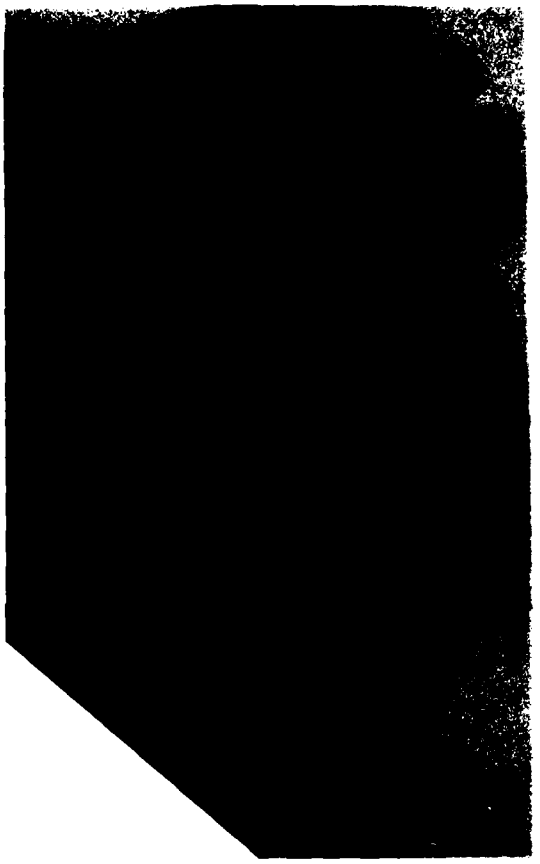

Figure 2

Figure 3

Figure 4

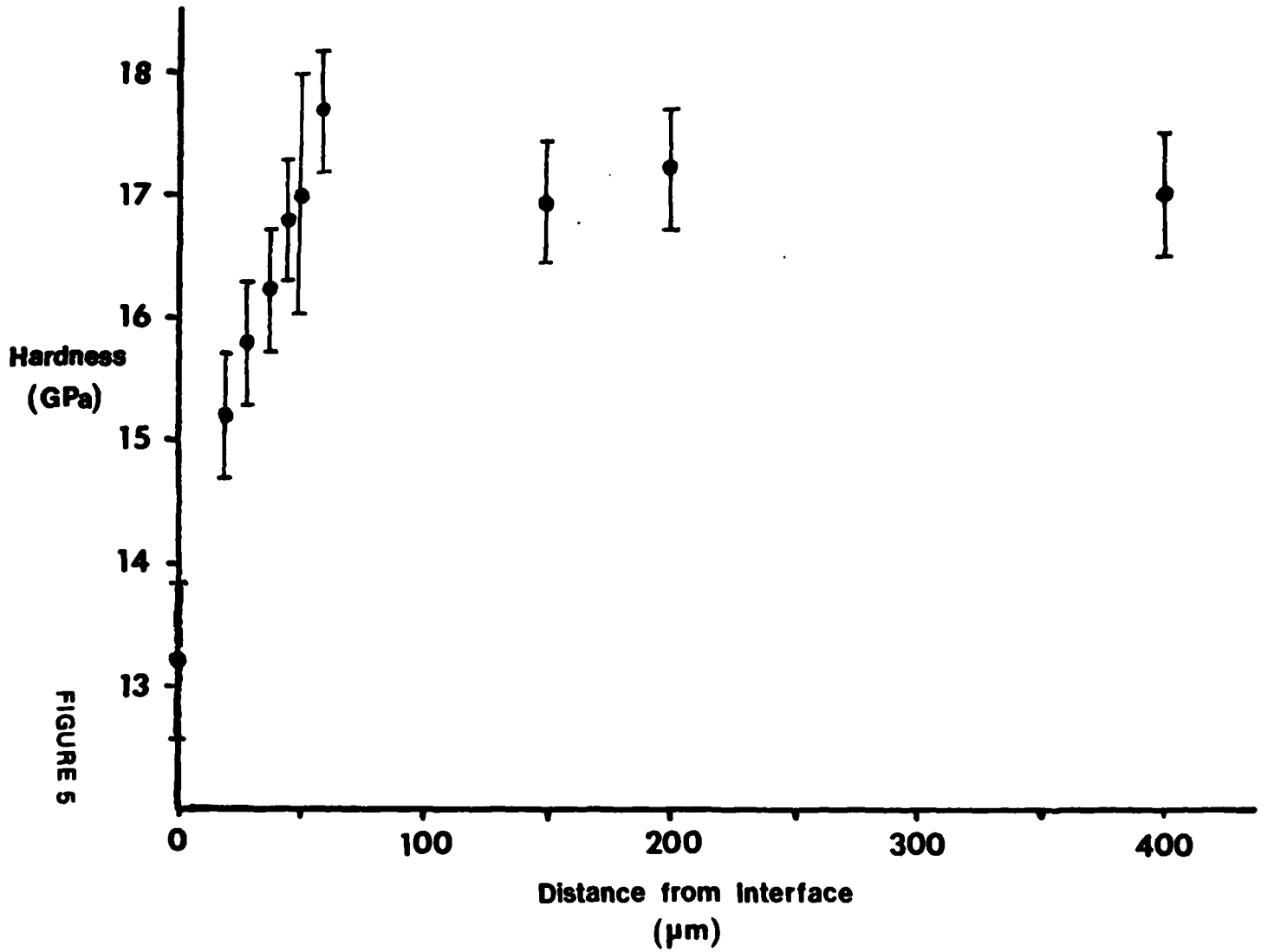
18
17
16
15
14
13
Hardness
(GPa)
0
100
200
300
400
Distance from Interface
(μm)

FIGURE 5

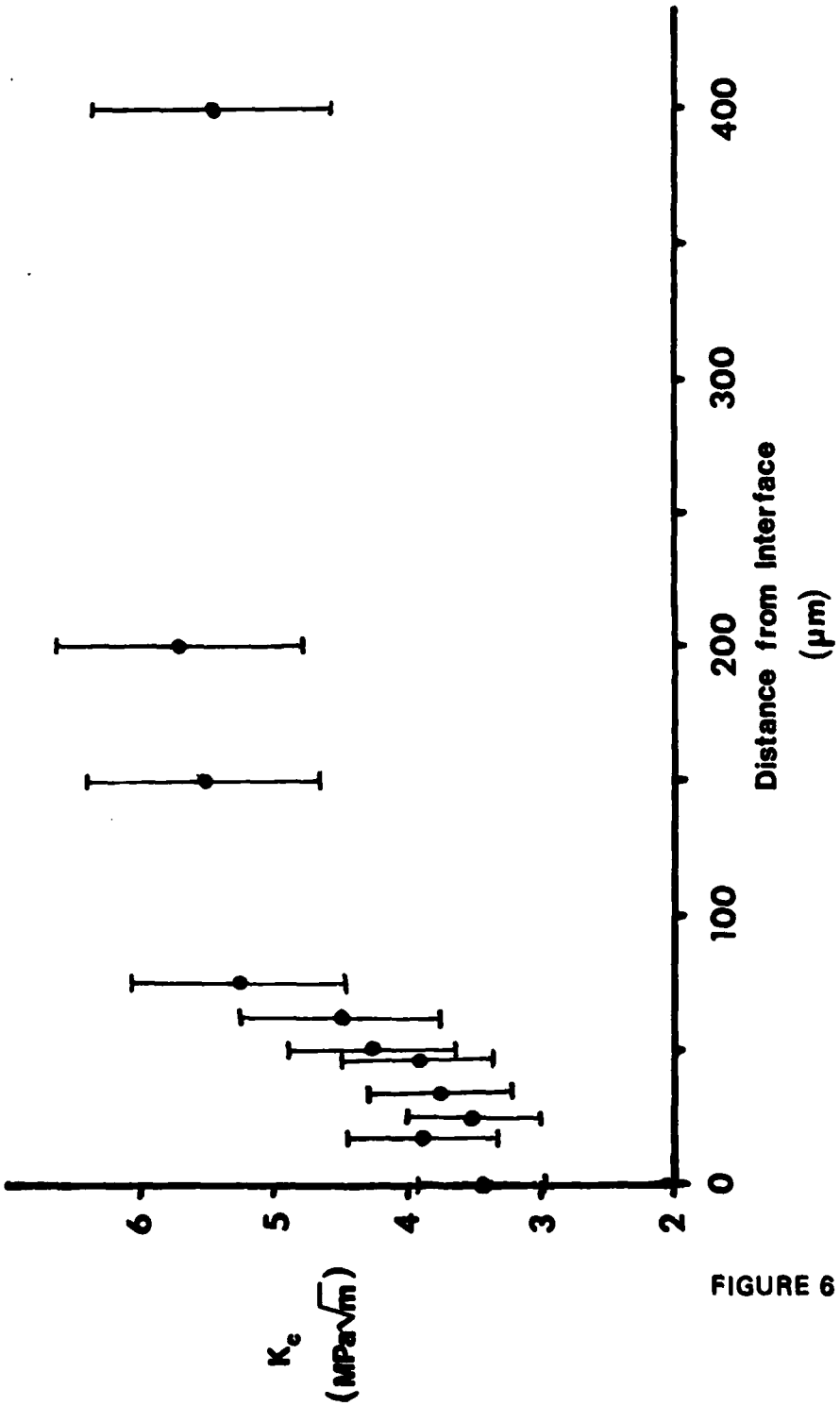
K_c (MPa$\sqrt{m}$)
6
5
4
3
2
0
100
200
300
400
Distance from Interface (μm)

FIGURE 6

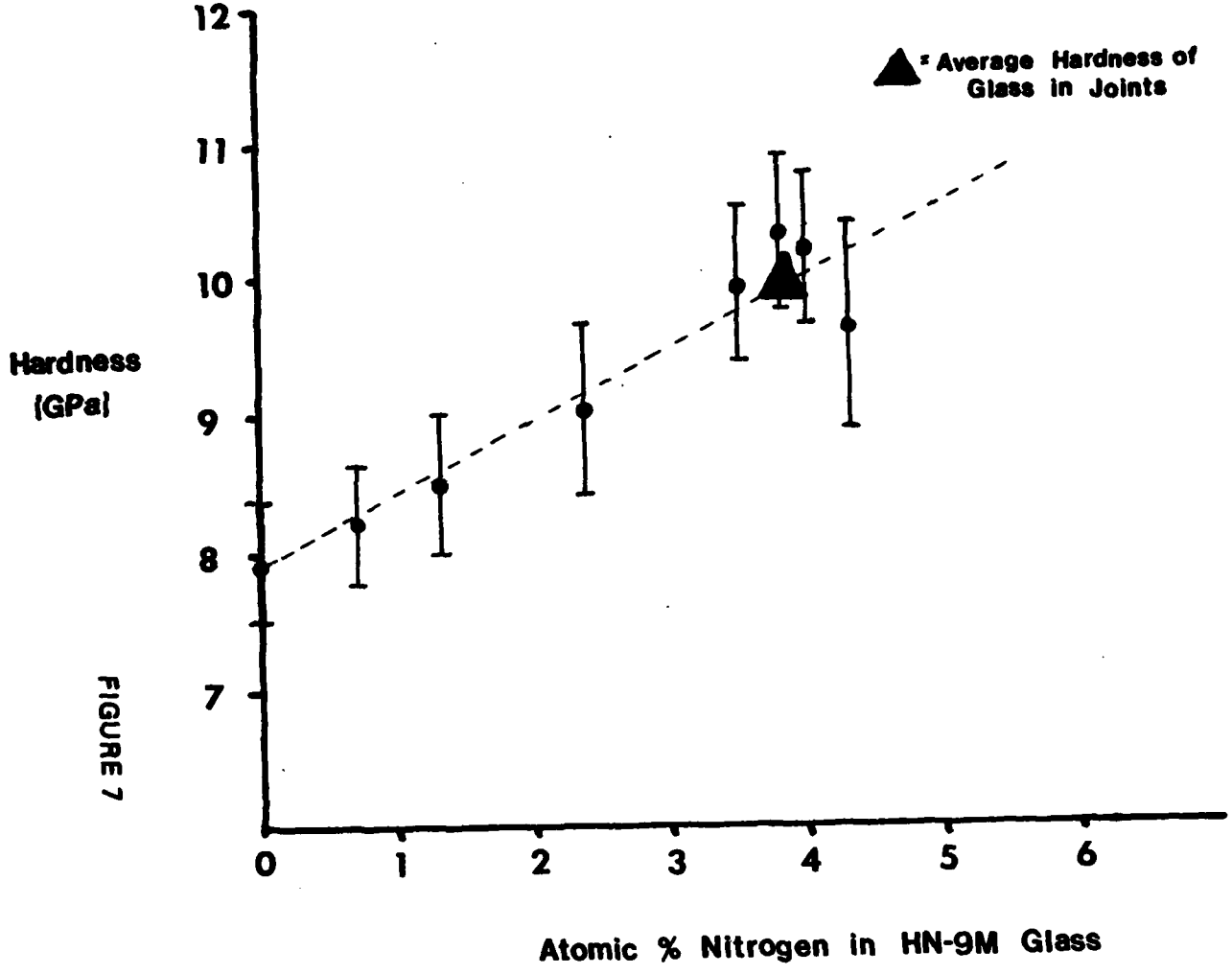
12
11
10
9
8
7
Hardness
(GPa)
▲ = Average Hardness of
Glass in Joints
0
1
2
3
4
5
6
Atomic % Nitrogen in HN-9M Glass

FIGURE 7

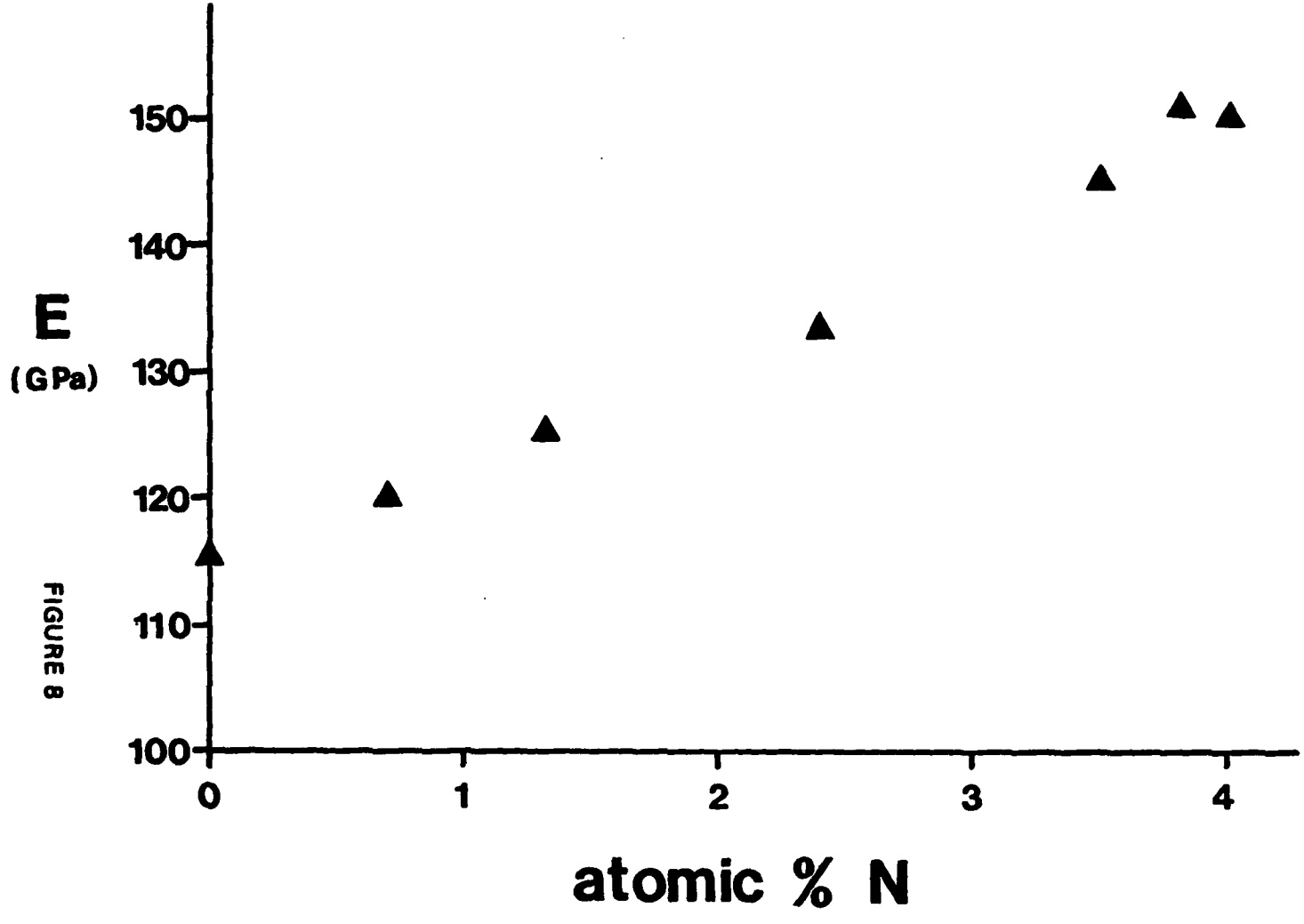

FIGURE 8

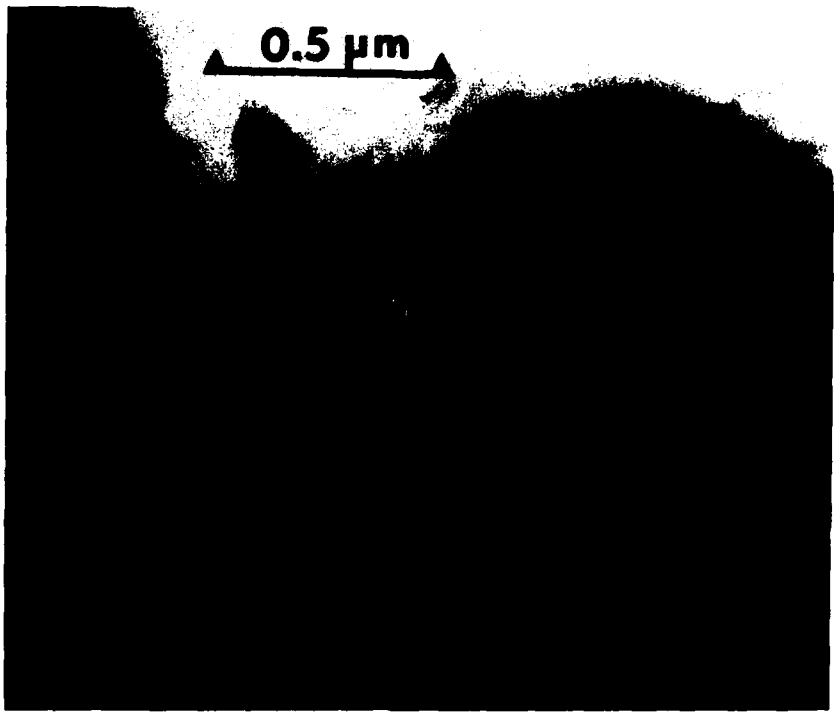

Figure 9

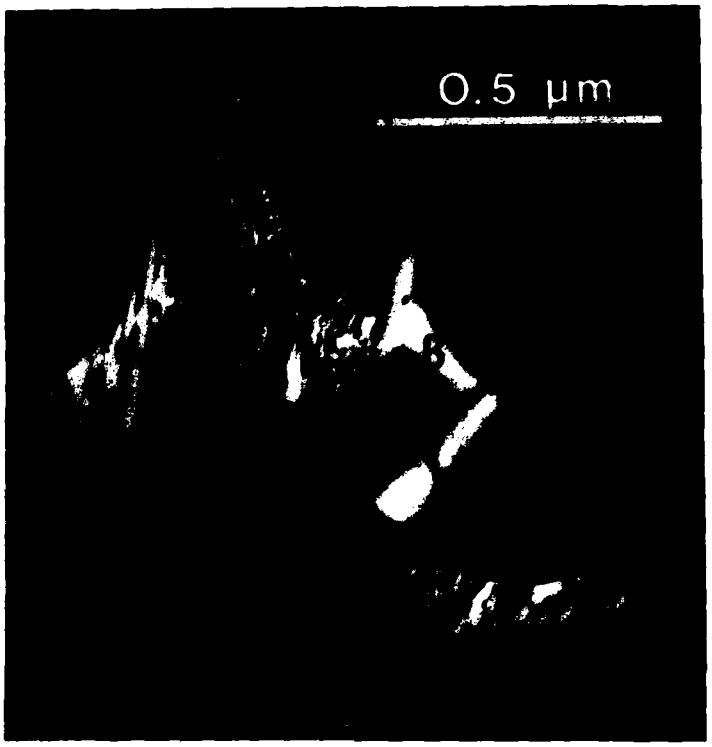

Figure 10

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